Pharm.

THE ANALYST

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THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

ORDINARY MEETING

An Ordinary Meeting of the Society, organised by the Physical Methods Group, was held at 7 p.m. on Wednesday, April 2nd, 1958, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the President, Dr. J. H. Hamence, M.Sc., F.R.I.C.

The subject of the meeting was "Gas Chromatography," and the following papers were presented and discussed: Introductory Talk by C. S. G. Phillips, M.A.; "Applications of Gas Chromatography in the Halogenated Hydrocarbon Field," by R. Hill, B.Sc., A.R.I.C.; "Gas Chromatography in the Petroleum Industry," by D. H. Desty, B.Sc.

NEW MEMBERS

Ordinary Members

Philip Atherton, A.R.I.C., A.R.T.C.S.; Thomas William Brandon, B.Sc. (Lond.), F.R.I.C.; Chuni Lal Chakrabarti, B.Sc. (Calcutta); Isaac Hodara, M.Sc. (Jerusalem); Edward Albert Hontoir, B.Sc., A.I.M.; Jeffery Michael Llewellin, B.A. (Cantab.); Fred Ridgway, B.Sc. (Lond.); Allan Neal Smith, M.Sc. (Dunelm.), A.R.I.C.; William John Williams, B.Sc., Ph.D. (Lond.).

Junior Member

Terence Dwyer, A.R.I.C.

DEATH

We record with regret the death of

Arthur Gordon Francis.

SCOTTISH SECTION

An Ordinary Meeting of the Section was held at 7 p.m. on Friday, February 28th, 1958, in the George Hotel, George Street, Edinburgh. The Chair was taken by the Chairman of the Section, Dr. Magnus Pyke, F.R.I.C., F.R.S.E.

A lecture on "The Solvent Extraction of Metal Complexes" was given by F. J. C. Rossotti, B.Sc., M.A., D.Phil.

MIDLANDS SECTION

The third Annual General Meeting of the Section was held at 6.30 p.m. on Tuesday, March 4th, 1958, in the Mason Theatre, The University, Edmund Street, Birmingham, 3. The Chair was taken by the Chairman of the Section, Dr. R. Belcher, F.R.I.C., F.Inst.F. The following appointments were made for the ensuing year:—*Chairman*—Dr. R. Belcher. *Vice-Chairman*—Dr. S. H. Jenkins. *Hon. Secretary*—Mr. G. W. Cherry, 48, George Frederick Road, Sutton Coldfield, Warwickshire. *Hon. Treasurer*—Mr. F. C. J. Poulton. *Members of Committee*—Messrs. A. S. Beidas, H. E. Brookes, W. T. Elwell, J. R. Leech, W. M. Lewis, Dr. Alison M. G. Macdonald, Messrs. R. Sinar and J. H. Thompson. Miss M. E. Tunnicliffe and Mr. H. J. Alcock were re-appointed as Hon. Auditors.

An Ordinary Meeting of the Section was held at 7 p.m. on Thursday, March 13th, 1958, in the Gas Showrooms, Nottingham. The Chair was taken by the Chairman of the Section, Dr. R. Belcher, F.R.I.C., F.Inst.F.

The following paper was presented and discussed: "The Analytical Chemistry of Synthetic Detergents," by W. B. Smith, B.Sc.

WESTERN SECTION

A JOINT Meeting of the Section and the South Wales Section of the Royal Institute of Chemistry was held at 6.30 p.m. on Friday, March 14th, 1958, at the Chemistry Department Lecture Theatre, University College, Singleton Park, Swansea. The Chair was taken by the Chairman of the Western Section, Mr. S. Dixon, M.Sc., F.R.I.C.

A lecture on "Sequestration and its Analytical Applications" was given by R. L. Smith, B.Sc., Ph.D.

MICROCHEMISTRY GROUP

THE Fourteenth Annual General Meeting of the Group was held at 6.30 p.m. on Friday, February 7th, 1958, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chairman of the Group, Mr. D. F. Phillips, F.R.I.C., presided. The following Officers and Committee Members were elected for the forthcoming year:—*Chairman*—Mr. D. F. Phillips. *Vice-Chairman*—Mr. F. Holmes. *Hon. Secretary*—Mr. D. W. Wilson, Department of Chemistry, Sir John Cass College, Jewry Street, Aldgate, London, E.C.3. *Hon. Treasurer*—Mr. G. Ingram. *Members of Committee*—Mr. E. Bishop, Mrs. D. Butterworth, Messrs. R. Goulden, J. A. Hunter, C. Whalley and C. L. Wilson. Dr. L. H. N. Cooper and Mr. H. Childs were re-appointed as Hon. Auditors.

The Annual General Meeting was followed by an Ordinary Meeting of the Society, organised by the Group.

PHYSICAL METHODS GROUP

THE sixty-first Ordinary Meeting of the Group was held at 6.30 p.m. on Tuesday, February 18th, 1958, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the Chairman of the Group, Mr. R. A. C. Isbell, A.Inst.P.

The subject of the meeting was "Solid-source Mass Spectrometry" and the following papers were presented and discussed: "Solid-source Mass Spectrometry—Instrumentation," by G. H. Palmer, B.Sc., A.Inst.P.; "Solid Analysis Using a Spark-source Mass Spectrometer," by R. D. Craig, B.Sc.; "Stable-isotope Dilution Analysis," by R. K. Webster, B.A. (see summaries below).

SOLID-SOURCE MASS SPECTROMETRY—INSTRUMENTATION

MR. G. H. PALMER described the techniques in mass spectrometry for the isotopic analysis of elements available as solids having very low vapour pressures. A comparison was made between furnace and thermal-emission ion sources and a description was given of how the latter source could be used in conjunction with a high-sensitivity ion collector to analyse sub-microgram amounts of material. The causes of error in the measurements were examined and methods for minimising these errors were described.

The main features were given of a modern instrument designed for rapid routine analysis.

SOLID ANALYSIS USING A SPARK-SOURCE MASS SPECTROMETER

MR. R. D. CRAIG described a spark-source mass spectrometer, type M.S.7, designed according to the geometry of Mattauch for use with either photographic or electrical detection, which had been developed for the general analysis of solids.

The instrument had been widely applied to impurity analysis with photographic plates as detectors. An exposure range of at least 10^6 to 1 could be attained, and the sensitivity was such that impurities down to the level of 0·01 p.p.m. could be detected in favourable cases.

The use of the technique for impurity analysis was indicated in four main fields of application: (*i*) general metallurgical problems (*e.g.*, steels; nimonic alloys), (*ii*) pure metals (*e.g.*, aluminium), (*iii*) reactor materials (*e.g.*, carbon) and (*iv*) semi-conductors (*e.g.*, silicon).

Stable-isotope Dilution Analysis

Mr. R. K. Webster said that the method of stable-isotope dilution had been used as early as 1935 for hydrogen determination, but for a number of years it had been restricted to the few elements for which enriched isotopes were available. The development of solid-source mass spectrometers and the use of electromagnetic separators to prepare enriched isotopes had permitted a large expansion of the method in the last ten years. The author described the basis of the method, its scope and its limitations. The method was very sensitive, and limits of detection in the range 10^{-8} to 10^{-12} g were feasible for many of the elements. It was also very specific, and one of its chief features was the nearly complete freedom from interference problems; as a result it was one of the more accurate general methods of trace analysis. The main drawback was contamination, either from reagents or from the atmosphere, and it was often this quantity that determined the sensitivity for a particular element. The value of the method seemed to lie in the determination of trace concentrations, or higher concentrations when only very small samples were available; it could also provide standards for other methods of analysis.

BIOLOGICAL METHODS GROUP

An Ordinary Meeting of the Group was held at 6.30 p.m. on Wednesday, February 19th, 1958, in the restaurant room of "The Feathers," Tudor Street, London, E.C.4. The Chair was taken by the Chairman of the Group, Dr. S. K. Kon, F.R.I.C.

A discussion on "The Stage at which a Biological Assay can be Replaced" was opened by W. L. M. Perry, O.B.E., M.D.

Obituary

JULIAN LEVETT BAKER

Julian Levett Baker, who edited *The Analyst* from 1907 to 1920, died at his home in Maidenhead on January 29th, 1958, at the age of 84.

Julian Baker was born in London on February 24th, 1873, and educated at the City of London School, to which he was unable to return after the Easter vacation of 1888, as he had been in contact with a case of scarlet fever. This proved actually to his advantage. Knowing that Julian was set on becoming a chemist, his father consulted R. J. Friswell, then managing chemist to the old dyestuffs firm of Brooke, Simpson and Spiller, and Friswell advised having the boy coached for the next entrance examination to Finsbury Technical College, where Meldola, who had formerly been on Friswell's staff, had recently succeeded Armstrong as Professor of Chemistry. The boy passed in, as he would not have done had he remained at school another term.

At Finsbury in the eighties, the chemical students had not only their professor to look to, for Meldola had on his staff Streatfeild and Castell-Evans. What the students thought of Streatfeild is shown by the institution of the Streatfeild lectures. If Castell-Evans was less spoken of, he was not forgotten, as was shown by M. O. Forster in the course of his 1938 Streatfeild lecture. M. O. Forster was a man of Baker's year and remained throughout his life one of the most intimate of Baker's friends. G. T. Morgan was Baker's senior by a year at Finsbury, but was another life-long friend. It was during Baker's time at Finsbury that Meldola invited E. R. Moritz, the well-known consulting brewer, to deliver five lectures on brewing, lectures subsequently embodied in a printed book and later translated into German.

Young Baker was kept at Finsbury for three years, the normal course in those days being of two years only, but he had been very young at entrance and was still under nineteen when he was appointed assistant chemist to the London Beetroot Sugar Association, under A. R. Ling, who subsequently became Professor of Brewing at Birmingham. Association with such a man as Ling was another piece of good fortune. Ling had been one of Armstrong's earliest pupils at Finsbury and Armstrong kept in touch with such of his old students as could be persuaded to engage in some research, so far as their other duties permitted. Thus Armstrong would drop into the laboratory of the Sugar Association and advise these young men as to what they might usefully do. So began that long intimacy with Armstrong that has led the writer of another obituary to state that Baker was one of Armstrong's students.

That he never was, but he was one of the people the old man welcomed even when he lay a sick man. At first Ling and Baker published work on the halogen derivatives of quinone, but their interest lay increasingly in the degradation of starch. They published one or two papers on this subject, but were not encouraged to work in this field, which some of their seniors thought should be reserved to Horace Brown.

In 1900 Baker, who had been for some time chief chemist to the Sugar Association, did what he had long hoped to do. He gained entrance to the brewing industry, being appointed chemist (at first, sole chemist) to Watney, Combe, Reid and Co. Before taking up this appointment, he spent some months in the laboratory of Adrian Brown, then Professor of Brewing at Birmingham, and thus began another life-long friendship.

His duty to his Company permitted him to publish many papers in the chemical and brewing journals. His services to his Company may be judged by outsiders by the facts that he deferred his retirement until after the war and that for many weeks he and his chairman, a near neighbour and as old as Baker, drove daily between Maidenhead and London when railway services could not be depended on. From 1920 until 1948, he edited the *Journal of the Institute of Brewing*.

Baker had been a Member of the Council of the Chemical Society and of the Institute of Chemistry as well as a Vice-President of the Society of Chemical Industry and of the Institute of Brewing. As Honorary Secretary of the London Section of the S.C.I. in 1905, he was largely responsible for the success of the (for those days) ambitious programme for the Annual Meeting of the Society in London. Those were days. Members went by launch to Woolwich, to be shown over the Arsenal, all the men of the party in frock coats and silk hats.

Baker was one of the few Finsbury men to be elected a Fellow of the City and Guilds of London Institute. Another honour that fell to him and gave him pleasure was the award of the Horace Brown Medal of the Institute of Brewing.

Aged 84, he would sometimes say, after visiting his London club, "I hardly saw a man I knew." But a generation ago, among a crowd of chemists, the writer remembers reflecting that "Baker seems to know everyone here and everyone knows Baker." No one who saw Baker at work in his laboratory, or for that matter in his garden, which he loved, can have failed to note that he had very nice hands.

He married Eveleen Daniels in 1901; she died in 1945. In 1948 he married Mrs. Catherine St. Paul, who died in 1956. He is survived by a daughter and two sons.

G. C. JONES

Recent Developments in Chelatometry*

BY RUDOLF PŘIBIL

(*Analytical Laboratory of the Czechoslovak Academy of Sciences, Jilská* 16, *Prague* 1, *Czechoslovakia*)

LESS than ten years have passed since Professor Schwarzenbach of Zürich surprised the analytical world with his volumetric determination of calcium and magnesium.[1] As is well known, this was based on the use of a standard solution of disodium dihydrogen ethylenediaminetetra-acetate—a reagent now known by a variety of names, the commonest being "Complexone" or EDTA. As indicators for these titrations, he suggested Eriochrome black T and murexide. Schwarzenbach not only thoroughly studied the physico-chemical properties of the reagent and its complexes, as well as of a number of related compounds, but also laid the foundations of a new branch of volumetric analysis—complexometry. The extent to which this unique new method underwent development and gained acceptance within a very short time is without parallel in the history of analytical chemistry. To-day, both the principles and the experimental techniques of complexometry are so widely known that it will surely be unnecessary for me to deal with these aspects.

In a certain sense, complexometry is now at the peak of its development. I have in mind the number of cations (or anions) that can be determined by this highly elegant method. Practically the whole Periodic System comes within its scope—except, naturally, for the rare gases, some few elements of the first, fifth and sixth groups, and beryllium, boron and

* Presented at the meeting of the Society on Tuesday, November 5th, 1957.

silicon. This very universality, however, on the other hand, seriously hampers attempts to determine a given metal in a more complex solution—a common requirement, for instance, in the analysis of alloys, ores, minerals and many similar materials.

Many theoretical analysts regard the universal nature of the method as a serious drawback, and they belittle its practical significance by pointing out that any complex-forming reagent might be used in a similar way, by reference to the obsolescent theory of functional analytical groups, and so on. However, it would be pointless in this lecture to polemize with those holding such views.

The main aim of complexometry at the present time is to find ways and means of carrying out complexometric titrations with the maximum of selectivity. The problem is best dealt with if we analyse the factors that may affect, or prevent, complex formation by individual metals in solution. The most important of these factors will no doubt be pH and the presence of strongly complex-forming agents in the solution.

Effect of pH on complex formation by EDTA

The stability of complexes formed by EDTA is expressed by their stability constant, defined as follows—

$$K = \frac{[MeY]}{[Me]\,[Y]} \qquad (1)$$

(The ionic charges are omitted here for the sake of simplicity.)

The stability constants (or complexity constants), many of which have been carefully measured by Schwarzenbach and his school under precisely defined conditions (for instance, in decinormal potassium nitrate solutions), are a good guide in comparing the relative stability of various complexes. The measured stabilities vary very greatly. The most unstable complexes are those of the alkaline-earth metals, with pK values hardly reaching 10. Next in the series are the complexes of manganese and bivalent iron (pK = 14). For the majority of metals, the pK values lie between 16 and 19. The most stable complexes appear to be those of bivalent mercury, with a pK of 21, scandium and thorium (pK = 23), and indium, ferric iron and tervalent vanadium (pK = 25).

The concentration term, $[Y]$, in equation (1) is only identical with the concentration of free complexone in alkaline solution of a pH greater than 12, where ethylenediaminetetra-acetic acid is practically fully dissociated to the quadrivalent anion Y^{4-}. At lower pH values, there will be an equilibrium between the individual ionic species formed by the progressive dissociation of EDTA so that the real concentration of Y^{4-} ions will be much lower than the concentration of free complexone. This must be taken into account in calculating the stability constants at any given pH. The relation between the concentration of the ion Y^{4-} and the concentration of free complexone in its dependence on pH is the so-called α_H function—

$$1 + \frac{[H]^4}{K_1K_2K_3K_4} + \frac{[H]^3}{K_2K_3K_4} + \frac{[H]^2}{K_3K_4} + \frac{[H]}{K_4} \qquad (2)$$

By dividing the stability constants defined by equation (1) by the value of α_H we get the so-called pH-dependent stability constants. (The calculated values of α_H for various values of pH are shown in Table I.) If we take it as established that the lowest stability constant that permits complexometric determination is 10^8, then we can, by applying the α_H function, readily derive the lowest pH value at which a given titration will still be practicable. Ringbom has plotted these values for individual cations in a curve that we shall refer to as Ringbom's curve. Their course is analogous to that of the function α_H and is shown in Fig. 1.

Ringbom's curve is very instructive. It not only permits us to estimate the lowest pH at which a given cation can be determined, but also to what extent any other cation will interfere with this determination. As a corollary, it also demonstrates that there are combinations of cations that will not be titratable in presence of each other however carefully the acidity is adjusted and maintained. The theoretical interpretation of Ringbom's curve is not, of course, precise. For instance, his calculations do not take into account the initial concentrations of the cations or the sensitivity of the indicator. However, the curve is useful for the practical worker.

From what I have said it might appear that the theory of complexometric titration is completely settled and that any complexometric problem might be solved by purely

mathematical considerations. Unfortunately, the situation is not so simple as that. The pH is not the only factor influencing the "useful" stability constant. There is a large number of further effects, which, with certain misgivings, we include in a further factor β. This covers, for instance, the ionic concentration of the solution, the effect of less polar solvents, the influence of competing equilibria involving the component ions of the complex and other effects. In practice these effects are so closely interconnected that it would be quite a waste of time to attempt their exhaustive physico-chemical treatment. For this reason, the effect of the factor β as a whole is evaluated purely empirically at present and is expressed in the accuracy of the results, the description of interfering effects, concentration limits for the ion being determined and so on.

TABLE I

CALCULATED VALUES OF α_H

pH	α_H	pH	α_H
0·0	21·18	5·4	5·69
0·4	19·59	5·8	4·98
0·8	18·01	6·0	4·65
1·0	17·20	6·4	4·06
1·4	15·68	6·8	3·55
1·8	14·21	7·0	3·32
2·0	13·52	7·5	2·78
2·4	12·24	8·0	2·26
2·8	11·13	8·5	1·77
3·0	10·63	9·00	1·29
3·4	9·71	9·50	0·83
3·8	8·86	10·0	0·45
4·0	8·04	11·0	0·07
4·4	7·64	12·0	0·00
4·8	6·84	13·0	0·00
5·0	6·45	14·0	0·00

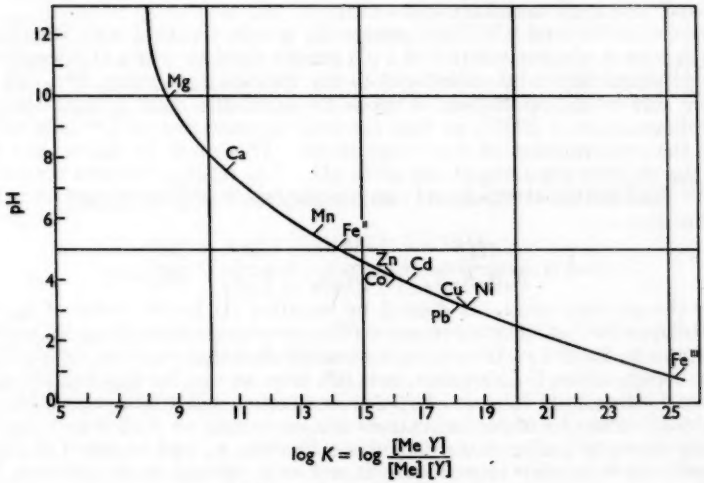


Fig. 1. Ringbom's curve

Let us return now for a moment to Ringbom's curve. As I have already pointed out, this curve indicates the pH that must be chosen to eliminate interference by as many other cations as possible. However, a further practical requirement is the availability of an indicator that will give a good end-point at the chosen pH.

Now, over the past three years much attention has been given to the question of complexometric indicators. More than one hundred compounds have been proposed for service as metal indicators in more or less specific instances. These compounds differ widely not

only in their chemical structure, but even in their mechanism of action. They include a number of well known and simple compounds that form complexes whose colour can be ascribed to the deformation of the cation; examples are the reaction of salicylic acid or tiron with iron. A further group of compounds may form coloured precipitates or colloidal solutions, or give rise to turbidity with certain cations or groups of cations. The largest group, however, are dyes that form soluble complexes differing in colour from the free dye; this group now includes also the "classical" indicators, Eriochrome black T and murexide; for this type of compound we have introduced the term "metallochromic indicator."

By reviewing the properties of these compounds we have arrived at certain conclusions regarding the structural pre-requisites of metallochrome action; these considerations in turn have stimulated the synthesis of a number of new compounds that have already proved themselves to be excellent indicators, with brilliant colour changes at the end-point. Our conclusions can be summarised in the following points—

All metallochromic indicators behave as acid - base colour indicators, under some conditions at least, even though they may not be used as such for one reason or other. In addition, however, the metallochromic indicators have marked complex-forming properties, which are entirely absent in the normal run of acid - base indicators. Moreover, the complex-forming grouping must be attached directly to the conjugated system of the dye.

We further observe that the change in colour induced in a metallochromic indicator on formation of a complex lies within the limits of the acid - base colour change. This indicates a fundamental relation between protonation or dissociation on one hand and formation of the complex on the other.

Our conclusions regarding the mechanism of action of metallochromic indicators, briefly speaking, give the following picture—

The colour changes of acid - base indicators are due to changes in the electronic structure of the dye system. If the auxochrome responsible for such colour changes in addition also forms part of a chelating group, then formation of a complex will lead to the same type of change in the electronic structure and hence also to the same kind of colour change.

This analysis indicates the points that should be borne in mind in searching for, or designing, new metallochromic indicators. Consideration along these lines led us to the conclusion that a dye system eminently suitable as a basis for the synthesis of metallochromic indicators was that of the sulphonphthalein and phthalein type; some azo dyes have also been examined in this respect. A suitable complex-forming group seemed to be the iminodiacetic acid grouping, which is in accord with Schwarzenbach's experience. Even the introduction of the aminoacetic acid (glycine) grouping has been found to confer marked metallochromic properties on acid - base indicators.

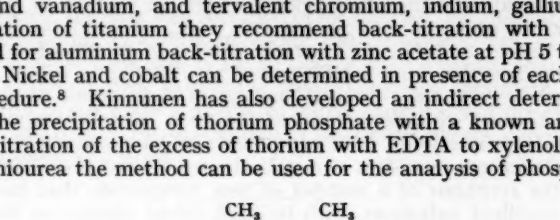
Some new indicators and their colour changes

Perhaps I might now briefly mention some of the new indicators and demonstrate their end-point colour changes.

Xylenol orange—

3:3′-Bis-di(carboxymethyl)aminomethyl-*o*-cresolsulphonphthalein (xylenol orange, **I**)[2,3] is obtained by the condensation of cresol red with formaldehyde and iminodiacetic acid. In acid solution up to about pH 5·6 to 6 it is yellow; in alkaline solutions it has a deep reddish purple colour. Its use as an indicator is therefore confined to the acid pH region. The colour transition at the end-point is extremely sharp, probably better than that of any other indicator proposed so far. The stability of the individual metal - indicator complexes is, of course, dependent on the acidity, so that a certain pH range must be maintained for each metal. So far, titrations with this indicator have been described for bismuth at pH 1 to 2, thorium at pH 2·5 to 3·5 and for lead, zinc, cadmium, lanthanum and scandium at pH 5 to 6, most conveniently in solutions buffered with hexamethylenetetramine. Excellent results have also been obtained in the titration of mercury,[4] and an indirect method is available for aluminium[5] based on the back-titration of the excess of complexone with zinc, lead or thorium salts. Kinnunen and Wennestrand[6] have shown that tin can be determined in its alloys with copper by back-titration with thorium, the copper being screened with thiourea.

The same authors, in unpublished work,[7] have also shown xylenol orange to be an excellent indicator for the indirect complexometric determination of iron, nickel, cobalt, copper, quadrivalent uranium and vanadium, and tervalent chromium, indium, gallium and thallium. For the determination of titanium they recommend back-titration with a thallium^{III} salt at pH 4·4 to 5, and for aluminium back-titration with zinc acetate at pH 5 to 6 in ammonium acetate solution. Nickel and cobalt can be determined in presence of each other by a relatively simple procedure.[8] Kinnunen has also developed an indirect determination of phosphate[7] based on the precipitation of thorium phosphate with a known amount of thorium nitrate and back-titration of the excess of thorium with EDTA to xylenol orange; if copper is screened with thiourea the method can be used for the analysis of phosphor bronzes.



(I)

Xylenol orange

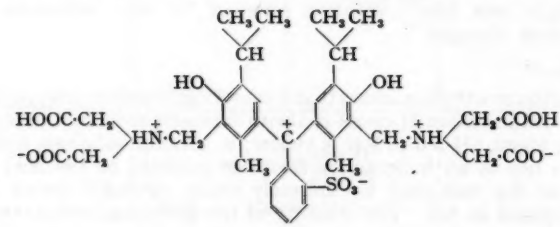
By suitable adjustments of the acidity, pairs of metals such as bismuth and lead, and bismuth and cadmium can be individually determined in a single solution.

Xylenol orange is used as a 0·1 to 0·5 per cent. aqueous solution, which is stable for several months; one or two drops of this solution are used for each titration.

METHYLTHYMOL BLUE—

3:3′-Bis-di(carboxymethyl)aminomethylthymolsulphonphthalein (methylthymol blue, **II**)[9,10] is prepared in the same way as xylenol orange, but from thymol blue as the starting material. This compound also retains the acid - base indicator properties of the parent dye; it is yellow in acid solution, turning light blue at pH 6·5 to 8·5 and grey at 10·5 to 11·6. Above pH 12·7 it forms a dark blue anion. It can not only be used in acid solution for titration of all cations mentioned under xylenol orange, but can also be used in strongly alkaline solution for alkaline-earth metals. Methylthymol blue undergoes a very sharp metallochromic colour change from yellow to blue, this being the maximum possible range of the visible spectrum.

The exceedingly wide pH range over which this compound functions as a metal indicator makes it possible to titrate to successive end-points in strongly acid, weakly acid and alkaline solution. Thus we can successively titrate bismuth, zinc and magnesium—a combination that frequently occurs in pharmaceuticals—or zinc and magnesium in alloys, and so on.



(II)

Methylthymol blue

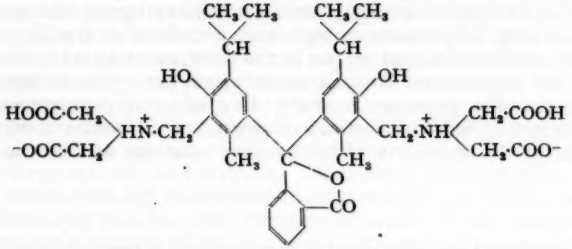
Another example is the evaluation of calcium ethylenediaminetetra-acetate injections —used as an antidote in lead poisoning—involving the titration of the excess of free complexone or calcium, and of the total complexone or calcium in a single solution.[11] The indicator can also be used for the titration of lead in urine, an important analytical index in the treatment of lead poisoning.

Aqueous solutions of methylthymol blue are not very stable and it is therefore more convenient to use an intimate mixture (1 + 100) with potassium nitrate.

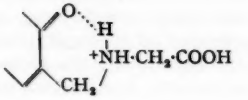
A number of further indicators having similar properties—xylenol purple, methylxylenol blue and others—can be prepared from other sulphonphthalein dyes; they have recently been listed in *Chemistry and Industry*.[12]

THYMOLPHTHALEXONE AND FLUOREXONE—

Another dye system suitable for use as a basis for the synthesis of new metallochromic indicators is the phthalein system. The Mannich condensation with iminodiacetic acid can again be used to introduce the chelating group. Owing to the presence of a rather stable lactone ring, these indicators operate only in alkaline solution. This is not to say that no complex formation takes place in acid solution, but the cation on entering into the chelate complex is not capable of forcing the lactone ring to open in order to form the coloured indicator ion. The first indicator of this group, Cresolphthalein Complexone or phthalein purple, was prepared by Schwarzenbach some years ago.[13] Its drawbacks as an indicator in the complexometric determination of strontium and barium are well known. The colour effect at the end-point is merely hypochromic, *i.e.*, there is a decrease in the intensity of the purple colour of the solution. The colour of the free indicator can be suppressed by the addition of alcohol, but this again may lead to precipitation, *e.g.*, of barium carbonate.

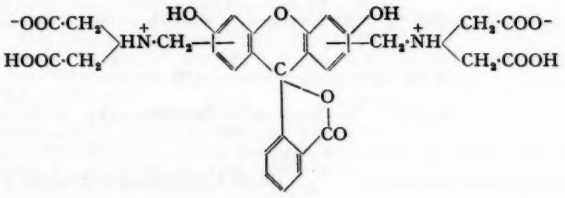


(IIIa)
Thymolphthalexone



(IIIb)
Glycinethymol blue

Our new indicator thymolphthalein complexone or Thymolphthalexone (**IIIa**),[14] which is the analogous derivative of thymolphthalein, has a great advantage in this respect. Its acid - base colour change lies at much more alkaline pH values, so that the end-point in the titration of alkaline-earth cations is marked by a sharp colour change from deep blue to greyish yellow or almost colourless. The corresponding derivative of phenolphthalein, Phenolphthalexone, is much less satisfactory.



(IV)
Calcein

A very interesting compound is the metal indicator derived in the same way from fluorescein. This compound was first obtained—though evidently in an impure state—by Diehl and Ellingboe[15] and has been marketed under the name Calcein. A much purer product has been obtained in our laboratories by Körbl and called Fluorexone.[16] The compound differs from the parent dye in showing in *acid* solution a green fluorescence that is quenched by alkali; however, the fluoresence reappears if traces of calcium are present. The end-point of a titration with complexone in alkaline solution is therefore marked by a quenching of the fluoresence, and the resulting solution is almost colourless or faintly pink, according

to the concentration of the indicator. Spectral measurements have shown that there is no change in colour at the end-point, but only a sudden change in fluorescence. Fluorexone is a suitable "metallofluorescent" indicator for the titration of calcium in strongly coloured solutions, and also serves for fluorimetric detection and determination of minute traces of the alkaline-earth metals.

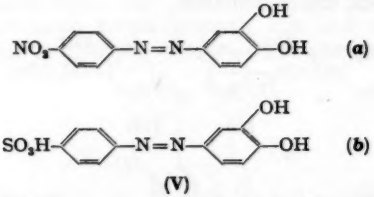
GLYCINETHYMOL BLUE AND GLYCINECRESOL RED—

In the synthesis of new indicators we are, of course, by no means limited to the chelating grouping formed by the phenolic hydroxyl group together with the iminodiacetic acid group. If other amino acids are used in the same type of synthesis, we obtain further indicators of much greater selectivity. For instance, we have prepared compounds containing a carboxymethylaminomethyl group in a suitable relationship to the phenolic hydroxyl group by using glycine in the Mannich condensation. The glycinethymol blue (**IIIb**)[17] obtained by applying this reaction to thymol blue is highly selective in its action. The removal of one of the carboxylmethyl groups of the original chelating grouping leads to a decrease in the range of cations with which the indicator will react, and to a displacement of the pH stability region of the complexes formed by others. In a weakly acid medium, the indicator will react with copper to give an intense blue colour. The reaction is very much more sensitive than that with ammonia or glycine alone. A very simple complexometric determination of copper can be based on this reaction. Complex formation between glycinethymol blue and nickel takes place very slowly and only in presence of high concentrations of the metal. We can therefore use the indicator to detect traces of copper in the presence of nickel, cobalt and other metals, and even for the colorimetric determination of copper. The recently prepared compound glycinecresol red also promises to have very interesting properties.

By varying the amino acid component in the condensation we get a whole series of very interesting derivatives, which differ in the sensitivity of their colour reactions and the rate of complex formation.

THE AZO-DYE INDICATORS—

The third dye system that we have used as a basis for the construction of metallochromic indicators is the azo-dye system. The simplest compounds having metallochromic properties are two indicators[18] in which the complex-forming grouping consists of two phenolic hydroxyl groups in *ortho* positions, *viz.*, 3:4-dihydroxy-4'-nitroazobenzene (**Va**) and 3:4-dihydroxyazobenzene-4'-sulphonic acid (**Vb**). As had been expected, these compounds resemble in many respects the indicator pyrocatechol violet, which has the same chelating grouping. They form coloured complexes with bismuth, thorium and copper, and may indeed serve as indicators in the complexometric determination of these metals.



(V)

(*a*) 3:4-Dihydroxy-4'-nitroazobenzene (*b*) 3:4-Dihydroxyazobenzene-4'-sulphonic acid

The condensation with iminodiacetic acid or glycine can also be carried out in this dye series. As examples I will mention naphthol violet[19] and glycinenaphthol violet,[20] which might find practical application to titrations in acid and alkaline solutions.

EFFECT OF FURTHER COMPLEX-FORMING COMPOUNDS

Permit me now to say a few words about the screening of cations in complexometric titrations. By using certain reagents capable of forming very stable complexes we can, in principle, screen a number of cations and thereby make these titrations more selective. This approach is certainly very tempting, but also rather difficult. The screening reagent must fulfil a number of conditions: it must form complexes that are many times more stable

than those formed with EDTA, the complexes should be colourless and water soluble, their formation should be quantitative at stoicheiometric ratios and should proceed without side reactions, and so on. Quite a number of such reagents are now known, but the use of most of them is limited to the alkaline pH region. The use for this purpose of potassium cyanide, ammonium fluoride,[21] triethanolamine,[22] 2:3-dimercaptopropanol[23] and other compounds was reviewed in an article in 1955.[24]

As I have mentioned, with the introduction of new metallochromic indicators it has become possible to move outside the alkaline pH region in complexometry. This leads not only to new possibilities, but also to new demands being made for screening reagents for this pH region. The state of affairs in this respect is by no means satisfactory yet. There is the possibility of screening iron by fluoride, copper by thiourea and mercury by thiosemicarbazide[25]; this last reaction in particular is highly selective and makes possible the indirect determination of mercury in the presence of practically all the other elements. As an example of the further possibilities that exist in this direction, I should like to show you a reaction that might make it possible to screen bismuth and thorium in the presence of zirconium: so far this is only in the qualitative stage.

From the theoretical point of view a number of objections can be raised to the screening of cations in solution. It would appear necessary to calculate equilibria in various complicated systems, take account of the indicator sensitivity and so on. In any case, this field of complexometry certainly deserves increased attention.

This account does not, of course, exhaust the possibilities of complexometry. In solutions of a complex qualitative and quantitative composition we cannot usually resort to complexometry without previous chemical treatment. By this I have in mind the separation, by some means or other, of various components of the solution. This can often be done by applying classical methods such as those established in gravimetric analysis, or more modern ones, such as extraction, ion exchange and so on. Here it is important to stress that such separations can frequently be speeded up considerably if we bear in mind the particular requirements and possibilities of complexometry. Often, for instance, it is quite unnecessary laboriously to achieve the complete separation of two components, but it is sufficient to reduce the concentration of the dominant component to such an extent that the residual amount can be dealt with by the usual methods of complexometry. This applies, for instance, to ion-exchange methods, which, incidentally, have not yet been applied in complexometry to any great extent. This and numerous other possibilities await development at the hands of analytical chemists.

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The Semi-micro Determination of Chlorine in Poly(Vinyl Chloride) and Related Polymers

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A semi-micro method has been developed for the determination of chlorine in polymers and copolymers of vinyl chloride.

A sample of the polymer is fused with sodium peroxide in a small electrically fired bomb. After dissolution of the melt, removal of excess of peroxide and acidification, the chloride is titrated with standard silver nitrate, use being made of an automatic titrimeter.

Recently we were called upon to develop a very rapid method for the semi-micro determination of chlorine in small samples of poly(vinyl chloride) and related polymers, *e.g.*, copolymers of vinyl chloride with vinylidene chloride or vinyl acetate. A method applicable to large numbers of samples at one time when the amounts of sample available for test are only about 20 mg was required. Methods such as the micro Carius test, which we have used for some time, were obviously inapplicable, owing to the rather long time required for the determination. Moreover, the method[1] developed by Soppet and one of us (J.H.) for the macro-determination of chlorine in polymers could not be used directly on the semi-micro scale, owing to the relatively high blank values as compared with sample titrations when a 15-g charge of sodium peroxide is used.

Attempts to apply Bather's method[2] on the micro scale to the problem were unsuccessful; the results were invariably low whatever concentration of sulphuric acid was used in the breakdown of the polymer with ammonium ceric sulphate and acid.

Ultimately, it was decided to reduce the macro method to the semi-micro scale. In doing so it was necessary, in co-operation with Messrs. Chas. W. Cook & Sons (University Works, Walsall Road, Birmingham), to design a small electrically fired bomb for sodium peroxide fusion, in which 20 mg of the polymer sample could quickly be broken down with 1 g of sodium peroxide. The bomb was made of stainless steel and the capacity of the cup was approximately 2 ml.

A thorough search of the literature carried out subsequent to our work has shown that Eger and Yarden[3] have designed a similar bomb of capacity 8 ml for the semi-micro determination of fluorine in organic fluoro compounds.

Further, in order to retain both speed and accuracy, it has been necessary to carry out the final titration of the ionised chloride with standard silver nitrate, use being made of an automatic titrimeter as described by Squirrell and one of us (J.H.).[4,5]

The small reference electrode used in this work consists of an 18 s.w.g. silver wire immersed in a solution containing a very slight excess of silver ions. The reference electrode is maintained in contact with the solution to be titrated by means of a ground-glass sleeve, which is kept moistened with the solution contained in the electrode vessel. The indicator electrode is an 18 s.w.g. silver wire. In order to avoid false potentials, this electrode is kept in a position touching the stirrer and is therefore continually vibrated during the titration. The silver nitrate is standardised against sodium chloride that has been fused with sodium peroxide in exactly the same way as the sample.

Method

Apparatus—

A diagram of the semi-micro bomb is given in Fig. 1 and of the reference electrode in Fig. 2. The automatic titrimeter used in this work was manufactured by Messrs. Electronic Instruments Limited.

Reagents—

Sodium peroxide—Sodium peroxide of low chlorine content (manufactured by Imperial Chemical Industries Limited) was used.

Starch catalyst—AnalaR soluble starch that had been heated for 3 hours at 100° C before use was used.

Nitric acid, concentrated—The AnalaR reagent was used.

Nitric acid, 2 N—Dilute 12·5 ml of concentrated nitric acid to 100 ml with water.

Sodium hydroxide solution, 10 per cent. w/v—Dissolve 10 g of sodium hydroxide in water, cool and dilute the solution to 100 ml with water. The AnalaR reagent was used.

Methyl red indicator solution—A 0·05 per cent. w/v solution in ethanol.

Silver nitrate solution, 0·02 N—Prepare by dilution of a 0·1 *N* stock solution.

Sodium chloride solution, 0·02 N—Prepare by dilution of a 0·1 *N* stock solution.

Sodium chloride—AnalaR sodium chloride that had been heated for 4 to 5 hours at 270° ± 10° C before use was used.

Reference electrode solution—Prepare a solution containing 64 ml of saturated sodium sulphate solution, 6·0 ml of 2 *N* nitric acid, 30 ml of 0·1 *N* sodium chloride solution and 30·1 ml of 0·1 *N* silver nitrate solution. Mix the solution and allow to stand until the bulk of the silver chloride has settled out. Fill the reference electrode with this solution.

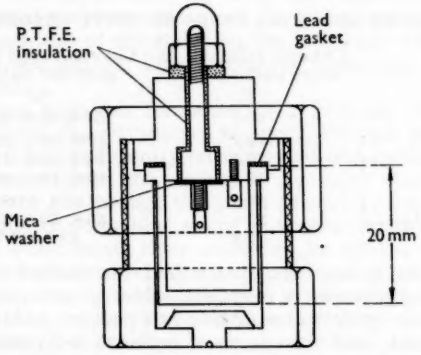

Fig. 1. Cross-section of semi-micro bomb

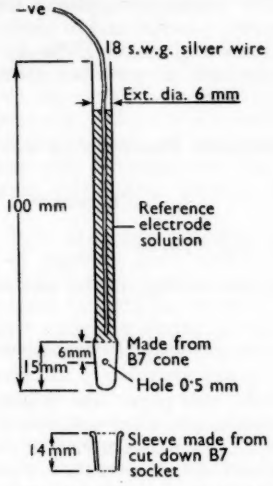

Fig. 2. Reference electrode

PROCEDURE—

Weigh 20 mg of the sample into the cup of the bomb and add 0·06 g of dried starch together with 1·0 g of sodium peroxide. Mix intimately the contents of the cup, fire electrically by using 3 cm of fuse wire and a current of 2 to 3 amperes and then allow to cool in a bath of distilled water. After fusion, place the cup and top in a 50-ml beaker containing 10 ml of distilled water and cover the beaker with a watch-glass. Warm the beaker carefully to assist dissolution. When the melt has completely dissolved, remove the top of the bomb and cup and carefully wash them with a minimum of distilled water. Bring the solution just to the boil and maintain for 15 minutes to destroy the excess of peroxide. After cooling, make the solution just acid by adding concentrated nitric acid dropwise from a burette, using methyl red as indicator, again cool, add a further few drops of methyl red indicator solution and make the solution slightly alkaline by adding 10 per cent. w/v sodium hydroxide solution. Neutralise the solution with 2 *N* nitric acid and add 0·25 ml of acid in excess. The volume of the solution will be about 30 ml at this stage. Titrate the chloride with 0·02 *N* silver nitrate solution to a pre-set end-point, using the automatic titrimeter with the FAST - SLOW change-over control set at 50 mV before the end-point is reached. In this titration, use a burette that has a fine capillary jet kept below the surface of the solution being titrated.

Carry out a blank determination on the reagents, omitting only the sample.

Determine the pre-set end-point by an initial manual potentiometric titration as follows. Measure 15 ml of 0·02 *N* sodium chloride solution into a 50-ml beaker and add 15 ml of distilled water. Acidify the solution with 0·25 ml of 2 *N* nitric acid and titrate with 0·02 *N*

silver nitrate solution, using the manual control of the titrimeter. When the end-point is approached, make additions of silver nitrate solution in 0·1-ml increments and note the millivolt readings after each addition. Note the potential difference at which $\frac{\Delta E}{\Delta V}$ plotted with respect to V is at a maximum, and use this as the pre-set end-point on the titrimeter. In our experience, the end-point is usually at a setting of about +60 mV.

When large numbers of determinations are involved, it is our practice to determine the pre-set end-point daily.

Standardise the 0·02 *N* silver nitrate solution against 20 mg of dried sodium chloride that has been fused with sodium peroxide and subsequently titrated with the silver nitrate solution in exactly the same way as described for the sample.

Results

The results of applying the proposed procedure to the determination of chlorine in poly(vinyl chloride) and to copolymers of vinyl chloride with vinyl acetate and with vinylidene chloride are given in Table I. For comparison, results of corresponding determinations by the micro Carius method are included.

Table I

Chlorine contents of various polymers and copolymers of vinyl chloride

Substance	Chlorine found by the micro Carius method, %	Chlorine found by the proposed method, %
Poly(vinyl chloride)	56·7	56·6, 56·6, 56·7
Copolymer of vinyl chloride with vinyl acetate	49·8	49·6, 49·9, 50·0
	48·5	48·4, 48·4, 48·8
	46·8	46·6, 46·7, 46·8
Copolymer of vinyl chloride with vinylidene chloride	57·2	56·9, 57·2
	59·8	59·8, 59·9, 59·9
	63·3	63·3, 63·7

Since this paper was originally prepared, it has been shown that the method can be extended to the determination of chlorine in copolymers containing chlorine and nitrogen. The result of the determination of chlorine in a copolymer containing 14·4 per cent. of nitrogen by the micro Carius method was 24·3 per cent., and the results of replicate determinations by the proposed method were 24·1, 24·2 and 24·3 per cent.

It is suggested that the method may find application in the determination of chlorine on the semi-micro scale in other materials.

We are indebted to Miss M. Clark for her assistance in this investigation.

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A Field Method for the Rapid Determination of Hydrogen Cyanide in Air

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A field test for determining small amounts of hydrogen cyanide in industrial atmospheres is based on formation of a Prussian blue colour on test paper impregnated with ferrous sulphate and sodium hydroxide. The test is specific for hydrogen cyanide. The behaviour of a number of possibly interfering gases has been investigated. The test is sensitive to slightly less than 1 p.p.m. of hydrogen cyanide in air and has an error of ± 10 to 20 per cent. The blue stains obtained are permanent. Test papers properly prepared and stored retain their activity for at least 10 months.

Two field tests for the detection and approximate estimation of hydrogen cyanide in air are described in "Methods for the detection of toxic gases in industry—Leaflet No. 2" (Department of Scientific and Industrial Research).[1] One of these, the benzidine - copper acetate test, has been widely used, but it has certain drawbacks, *e.g.*, difficulty in controlling the critical moisture content of the test paper, instability of the reagents, of the prepared test paper and of the stains on the test paper after treatment with hydrogen cyanide, and lack of specificity. The alternative Congo red - silver nitrate test shares some of these drawbacks.

Tests based on formation of a Prussian blue colour from hydrogen cyanide, which would have the advantages of specificity and permanence of pigment, have usually been regarded as insufficiently sensitive and unsuitable for use as field tests.[2] Gettler and Goldbaum[3] determined the amount of hydrogen cyanide in solutions by aerating at 90° C and passing the gas through test paper previously impregnated with ferrous sulphate and sodium hydroxide to form blue stains of various intensities. These authors claimed that the test papers would retain their usefulness for several weeks if stored in a cool dark place. Our tests showed, however, that test papers prepared as described were sometimes unsatisfactory, and that anyway the papers could not be relied upon to retain their full activity after a few hours. We finally succeeded in establishing the conditions necessary for a test based on formation of a Prussian blue colour, which was free from the various drawbacks already mentioned.

Experimental

Test papers—

The success of the method depends largely on the correct preparation and storage of the test papers. These are prepared by immersing filter-paper in ferrous sulphate solution, drying, immersing in sodium hydroxide solution and again drying.

Reactions within the test paper—The two reagents that are incorporated in the test paper can react with each other and with atmospheric carbon dioxide or oxygen. Ferrous hydroxide, which is initially formed by the action of sodium hydroxide on the ferrous sulphate, can be preserved for long periods in spite of a reputation for instability. Shipko and Douglas[4] have shown that ferrous hydroxide in contact with saline solution containing either excess of hydroxide or of ferrous ions is stable for periods up to 6 months if oxygen is rigorously excluded. When the dried paper already impregnated with ferrous sulphate is soaked in alkali solution, about 50 per cent. of the sulphate ion passes into the solution. Only a few per cent. of the ferrous iron on the paper is oxidised to ferric iron during both this procedure and the subsequent drying of the paper. The sodium hydroxide on the test paper will readily absorb carbon dioxide, which has an inhibitory effect on the subsequent formation of the blue stain. In fact, if the test papers after impregnation with sodium hydroxide are allowed to dry in air, as recommended by Gettler and Goldbaum,[3] sufficient atmospheric carbon dioxide may be absorbed to cause faulty stains to be obtained later. This risk can be reduced by careful drying under an infra-red lamp, but can only be completely eliminated by drying in a vacuum-desiccator. The dried papers can be stored by inserting them in glass tubes, which are then sealed under vacuum. Papers so stored have an effective life of at least 10 months. Test papers should be used within 1 hour of preparation or of withdrawal from storage tubes.

Penetration of the stain—Cross-sections of test papers that had been used in the detection of hydrogen cyanide were examined under a microscope. Paper that had been freshly prepared showed a deep blue stain on the exposed face extending inwards for a distance approximately equal to two or three times the fibre diameter; beyond this point the paper was colourless. On the other hand, paper the upper face of which had been exposed to carbon dioxide before use in the field test showed only a faint blue colour that penetrated 30 to 50 μ inwards from the exposed face, and had a band of more intense blue in the central region of the cross-section. It is clear that, unless the whole of the hydrogen cyanide in the sample is trapped on the surface of the test paper, *i.e.*, within a depth of about 20 μ, depending on the texture of the paper, the amount of gas present cannot be properly estimated by visual examination of the stain. The importance of an adequate concentration of reagents in the test paper and of proper protection of the critical outside layer before use is obvious. It was found that the proposed method of preparation produced test papers of average composition 10 mg per sq. cm of Whatman No. 50 filter-paper, 0·3 mg per sq. cm of total iron (including at least 50 per cent. as ferrous iron), as Fe, 0·2 mg per sq. cm of sulphate, as SO_4, and 4·5 to 5·5 mg per sq. cm of alkali, as sodium hydroxide. Papers of this composition were invariably satisfactory. Occasionally, satisfactory stains were obtained with papers containing as little as either 0·05 mg per sq. cm of ferrous iron or 1 mg per sq. cm of sodium hydroxide.

SAMPLING RATE—

In order to obtain an even coloured stain it is essential that the rate of flow of gases passing through the test paper does not exceed 6 ml per second. It is very difficult to maintain this slow steady flow with a hand pump, and even occasional bursts of speed can result in pin points of deep blue colour on the test paper where the gas has streamed through larger pores. The use of a rubber-bulb aspirator avoids this difficulty.

CALIBRATION OF STAINS—

To prepare standard stains, a stream of air mixed with hydrogen cyanide in the desired proportions was prepared as described by McKelvey and Hoelscher.[5] The hydrogen cyanide was supplied from a gas cylinder. Alternatively, a static concentration of mixed gases was prepared by sucking a stream of air into an evacuated 10-litre bottle together with the hydrogen cyanide liberated by the action of concentrated sulphuric acid on a known amount of 0·05 per cent. w/v potassium cyanide solution. The concentration of hydrogen cyanide in the mixed gases was determined by taking samples in an evacuated 2-litre flask containing 0·05 *N* sodium hydroxide. After prolonged shaking an aliquot of the alkaline liquor was withdrawn by pipette and analysed by the Lubatti method.[6] The results were checked occasionally by the Liebig argentimetric method, the end-point being determined photoelectrically. A series of five standard stains representing 2·5, 5, 10, 20 and 50 p.p.m. of hydrogen cyanide in a 360-ml sample was found to be adequate.

METHOD

APPARATUS—

Aspirator—A rubber-bulb hand aspirator of approximately 120-ml capacity was used.

Test-paper holder—A suitable form of holder is shown in Fig. 1. The paper is placed between two smooth-faced rubber washers held in position by two parallel brass plates carrying wing-nuts and bolts. Plates and washers are drilled to take a hole of 1 cm diameter and the sampled air enters inlet tube A to pass through the paper and leave by the outlet tube, B.

Dish—A glass, porcelain or plastic dish of about 200 ml capacity was used.

Glass tube containers for test papers—These were about 6 cm long and of 6 mm internal diameter.

Filter-papers—Whatman No. 50 filter-paper in sheets approximately 4 inches × 3 inches was used.

REAGENTS—

Ferrous sulphate solution—A 10 per cent. w/v aqueous solution of analytical-reagent grade hydrated ferrous sulphate.

Sodium hydroxide solution—A 20 per cent. w/v aqueous solution of analytical-reagent grade sodium hydroxide free from carbonate.

Sulphuric acid, 30 per cent. v/v.

PREPARATION OF THE TEST PAPERS—

Immerse a sheet of filter-paper for at least 5 minutes in a shallow vessel containing about 100 ml of ferrous sulphate solution. Remove the filter-paper and dry it by suspension over a radiator. The paper should then be white or off-white in colour. Cut off and discard a strip 2 cm wide from the lower edge of the filter-paper and cut the remainder of the sheet into rectangular pieces of 3·5 cm × 2·5 cm. Immerse the pieces of paper singly in the sodium hydroxide solution for about 15 seconds. Remove the papers, partly dry them with absorbent paper and transfer them quickly to a vacuum-desiccator. Evacuate the desiccator and leave the papers until they feel dry to the touch, but are not brittle. Satisfactory papers are greyish green to pale brown in colour.

For storage, vacuum seal each test paper in a piece of glass tubing.

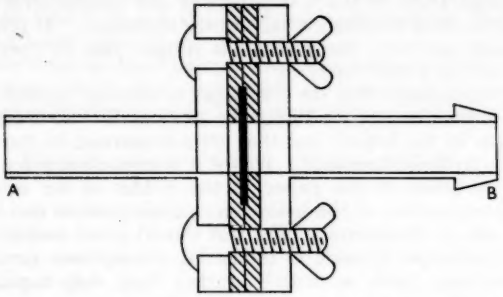

Fig. 1. Test-paper holder: A, inlet tube; B, outlet tube

PROCEDURE—

Break the sealed glass tube and remove the test paper. Fix the test paper between the rubber washers of the test-paper holder and screw up the two wing-nuts until they are finger-tight. Attach the holder to the aspirator by means of a piece of rubber tubing and draw the sample of air through the paper at a rate not exceeding 6 ml per second until 360 ml have passed. Remove the test paper from the holder and immerse it in 30 per cent. sulphuric acid contained in the dish. If hydrogen cyanide is present a blue colour develops on the paper in 30 seconds to 1 minute and an approximation of the hydrogen cyanide content of the atmosphere can be made by reference to the stain chart while the test paper is still in the dish. For a more accurate determination, remove the paper from the dish, wash it well with water, dry it and compare it with the stain chart.

DISCUSSION OF THE METHOD

SPECIFICITY—

The Prussian blue reaction is specific for hydrogen cyanide and the test papers are not stained blue except by this gas or by substances that could react to produce the cyanide ion, *e.g.*, cyanide dust or cyanogen. Cyanide dust can be removed from the gas sample before passage through the test paper by means of a cotton-wool filter. Neither hydrogen chloride nor ammonia appears to interfere with the test even when present in concentrations up to 400 p.p.m. Sulphur dioxide and hydrogen sulphide in amounts less than 50 p.p.m. do not appreciably affect the colour of the stain. Hydrogen sulphide can, if required, be removed by interposing a dry lead acetate paper in front of the hydrogen cyanide test paper in the holder. Chlorine inhibits the reaction of the test papers with hydrogen cyanide; if chlorine is likely to occur in the atmosphere under examination a qualitative test should be carried out.

SCOPE—

The test is sensitive to slightly less than 1 p.p.m. of hydrogen cyanide in air.

There is little difficulty in comparing stains as the background colour is white and the stains themselves differ only in the intensity of a single colour. With the recommended

series of standard stains, the error is estimated to be about ±10 per cent. for concentrations of hydrogen cyanide above 10 p.p.m. and about ±20 per cent. for concentrations below 10 p.p.m.

By increasing or reducing the volume of sample, the concentration range of hydrogen cyanide that can be covered is about 1 to 500 p.p.m.

The blue stains are permanent, and, after having been thoroughly rinsed and dried, test papers can be kept for reference purposes. Care should be taken to keep them out of contact with alkalis. They are unaffected by further exposure to an atmosphere containing hydrogen cyanide.

Papers can be safely used within 1 hour of preparation or of breaking the protective seal. No decrease has been detected in the activity of papers kept in vacuum-sealed glass tubes for at least 10 months.

Although the preparation of the test papers is not complicated and involves the use of fairly stable reagents, it is definitely a laboratory operation. If previously prepared and sealed papers are used, however, the method is simple, can be operated wholly by hand and is suitable for use as a field test.

The test has the advantages that the test paper is virtually unaffected by small amounts of hydrogen cyanide in the atmosphere during the 30 seconds or so needed to break the sealed tube and put the paper in the holder, and that after immersion in the acid bath the stained paper is unaffected by hydrogen cyanide. Hence it is unnecessary for the operator to be in fresh air either for insertion of the paper in the holder or for subsequent examination of the stain. An approximation of the hydrogen cyanide content can be made in 6 minutes and a more accurate one in 10 minutes. The test should prove useful for the determination of small amounts of hydrogen cyanide in industrial atmospheres generally, and also when it is required to determine fairly accurately, rather than very rapidly, concentrations of residual hydrogen cyanide.

This work was carried out on behalf of the Committee on Tests for Toxic Substances in Air, and the Ministry of Labour and National Service.

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The Determination of Copper in Gelatin

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Some newer methods for the determination of traces of copper have been applied to gelatin and results are compared with those obtained by present procedures; the advantages over the use of substituted dithiocarbamate-type reagents are discussed. The preferred procedure is with 2:2'-diquinolyl as reagent.

Traces of impurities in raw materials may have profound effects on photographic emulsions. It is desirable to have a method capable of determining the copper content of various gelatins in the range 0 to 15 p.p.m. The method to be selected had to fulfil the following conditions—

(*i*) the reagents to be used should be readily available in a reasonably pure state;
(*ii*) the procedure should be specific, yet simple and sensitive;

(*iii*) it should preferably involve an extraction stage; the partition coefficient should be high in favour of the organic phase;

(*iv*) the coloured complex produced should be stable, especially to light.

The reagents used in well known methods and their shortcomings may be summarised as follows—

Dithizone is non-specific,[1] unstable and has an intense colour of its own.

Sodium diethyldithiocarbamate is used in the British Standards method.[2] It is less sensitive than dithizone[1] and is not specific. An extraction stage into chloroform or carbon tetrachloride is often used, but the partition coefficient is small. The complex with copper is unstable to light.[3] This type of reagent has been used in conjunction with ethylenediaminetetra-acetic acid to increase specificity,[4,5] but interference still occurs.

Zinc dibenzyldithiocarbamate also suffers from non-specificity[6] and instability of the complex with copper to light. It has the advantage over sodium diethyldithiocarbamate that it can be used at a lower pH.

More recently, other methods have become available, some of which have been examined. These include methods in which 2:2′-diquinolyl, bis*cyclo*hexanone oxalyldihydrazone or 2:9-dimethyl-1:10-phenanthroline is used. Polarographic methods have also been examined.

Method of destroying organic matter

Reagents—

All reagents should be of recognised analytical grade.

Nitric acid, concentrated.

Perchloric acid, 72 per cent.

Sulphuric acid, concentrated.

Procedure—

Heat 2 g of gelatin and 10 ml of nitric acid in a 100-ml conical flask on a hot-plate until vigorous evolution of brown fumes occurs.[7] It is advisable to remove the flask from the hot-plate at this stage. Add 2 ml of sulphuric acid and continue heating until no more brown fumes are evolved and charring begins. Add 4 ml of perchloric acid and continue heating until the liquid is colourless or very pale yellow and then maintain the solution at the same temperature for a further 3 to 4 hours to ensure the removal of excess of perchloric acid. Little attention is required at this stage and several digestions can be conducted simultaneously. After the solution has cooled, dilute with about 10 ml of water, boil for a few minutes and then cool. The solution is now ready for the determination.

Colorimetric methods

All colorimetric measurements were made with a Gallenkamp photo-electric colorimeter.

With 2:2′-diquinolyl as reagent—

2:2′-Diquinolyl gives a magenta-coloured complex with cuprous copper, which can be extracted into *iso*amyl alcohol. *iso*Amyl alcohol is said[8] to give a slightly greater colour intensity than *n*-amyl alcohol. The complex of 2:2′-diquinolyl with cuprous copper is remarkably stable to atmospheric oxidation.[9] The partition coefficient is large[10] and is relatively slightly affected by high salt concentrations. The solubility of *iso*amyl alcohol in water at room temperature is appreciable, hence temperature control is desirable at the extraction stage. The reagent is sensitive to oxidising agents that may occur in the *iso*amyl alcohol or remain after the digestion with perchloric acid.[11] The alcohol is subjected to the pre-treatment described later and the digestion is prolonged to overcome these effects. It is claimed[12] that the extraction and reduction stages can be combined by adding the solvent dimethylformamide to the solution, but we have preferred to retain the advantages of extraction.

Reagents—

2:2′-Diquinolyl solution—A 0·02 per cent. w/v solution of analytical-reagent grade 2:2′-diquinolyl, m.p. 196° C,[13] in *iso*amyl alcohol. The commercial grade reagent, m.p. 186° to 192° C was also used without recrystallisation. According to Dr. J. Hoste the solution is stable for several months if stored in a brown bottle.

iso*Amyl alcohol*—Analytical-reagent grade, b.p. 128° to 132° C. This was treated before use in accordance with a communication from Dr. J. Hoste, as follows. An 800-ml portion was shaken with 100 ml of a 10 per cent. solution of sodium metabisulphite, the layers were separated and the alcohol layer was dried overnight in contact with anhydrous magnesium sulphate. After filtration, the alcohol was distilled and the fraction boiling over the range 128° to 132° C was collected and stored in a brown bottle.

Tartaric acid solution, 50 per cent. w/v.

Hydroxylamine hydrochloride solution, 15 per cent. w/v—Prepare freshly each week.[8]

Sodium hydroxide solution, 30 per cent. w/v.

Procedure—

After digestion to destroy the organic matter, treat the solution with 2 ml of tartaric acid solution and 2 ml of hydroxylamine hydrochloride solution. Adjust the pH to between 4 and 7 with sodium hydroxide solution (test by spotting micro drops on pH papers). Dilute the solution to 50 ml and transfer it to a thermostatically controlled water bath at 25° ± 0·5° C for 10 minutes. Add 10 ml of 2:2′-diquinolyl solution, also at 25° C, and shake the mixture for 3 minutes. Separate the organic layer and measure its optical density, using an Ilford No. 625 filter.

Results—Calibration curves with simple aqueous copper solutions and with known additions of copper to a de-ionised copper-free gelatin are shown in Fig. 1. The displacement of one curve from the other is due to copper in the digesting acids and the sodium hydroxide used for neutralisation.

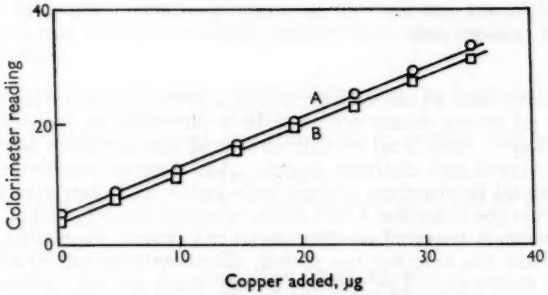

Fig. 1. Calibration curves for copper by 2:2′-diquinolyl method: curve A, digested with gelatin; curve B, no digestion

WITH BIS*cyclo*HEXANONE OXALYLDIHYDRAZONE AS REAGENT—

This reagent gives a blue colour with copper in the pH range 7 to 9 and, so far as is known, it is not extractable. It is highly specific for copper[14] and has been used for determining copper in paper and pulp[15] and in plants.[16] Citrate is added to prevent precipitation of the metal hydroxide.

Reagents—

*Bis*cyclo*hexanone oxalyldihydrazone solution*—A 0·5 per cent. w/v solution in 50 per cent. ethanol, warmed to dissolve the solute and filtered before use. This solution should be freshly prepared each day.

Ammonium citrate solution, 10 per cent. w/v.

Ammonia solution, sp.gr. 0·880—Analytical-reagent grade.

Neutral red indicator solution, 0·05 per cent. w/v.

Sodium hydroxide solution, 50 per cent. w/v.

Hydrochloric acid, concentrated—Analytical-reagent grade.

Procedure—

Prolonged digestion is not necessary and, after a clear solution is obtained, heating for 1 hour is sufficient. After it has cooled, transfer the solution to a 25-ml calibrated flask, add 0·5 ml of ammonium citrate solution and 4 drops—about 0·15 ml—of ammonia solution

and then 1 drop of indicator. Adjust the pH with sodium hydroxide or hydrochloric acid until the solution is just yellow (pH 7 to 9). Cool the solution frequently to minimise loss of ammonia. Add 1 ml of bis*cyclo*hexanone oxalyldihydrazone solution and dilute to the mark. Measure the optical density after 15 minutes, using an Ilford No. 626 filter. Occasionally, cloudy solutions are obtained, which require filtration into the colorimeter cell. The calibration curves obtained in this way resemble those shown in Fig. 1.

WITH 2:9-DIMETHYL-1:10-PHENANTHROLINE (NEOCUPROINE) AS REAGENT—

This reagent gives a yellow colour with cuprous copper under similar conditions to those used for 2:2′-diquinolyl. It has been used for determinations of copper in paper[17] and tungsten.[18] It is subject to the same interference from oxidising agents and the complex is extracted by the same solvent. It is advisable[17] to store the reagent solution in a refrigerator.

Reagents—

Buffer solution, pH 5—Dissolve 57 g of anhydrous sodium acetate and 17·0 ml of glacial acetic acid in water and dilute almost to 1 litre. Adjust the pH to 5·0 and then dilute to 1 litre.

Neocuproine solution—Dissolve 75 mg of 2:9-dimethyl-1:10-phenanthroline in 100 ml of buffer solution with vigorous shaking. Store the reagent in a refrigerator.

Ascorbic acid.

Tartaric acid solution, 50 per cent. w/v.

Procedure—

After digestion, add 2 ml of tartaric acid solution. Adjust the pH to approximately 5, and add 10 ml of buffer solution. Treat the solution with 3 ml of neocuproine reagent and about 50 mg of solid ascorbic acid, dilute to about 50 ml and then place the solution in a thermostatically controlled water bath at 25° ± 0·5° C for 10 minutes. Add 10 ml of *iso*amyl alcohol (purified as for use with 2:2′-diquinolyl), also at 25° C, and shake the mixture for 3 minutes. Separate the alcohol layer and measure its optical density, using an Ilford No. 622 filter.

POLAROGRAPHIC METHOD

A polarographic method in which dry oxidation is used has been described.[19] However, dry oxidation is not suitable for gelatin. The material froths considerably, and, on burning, leaves a mass of porous carbon, which is only slowly oxidised. The operation is tedious and requires considerable attention from the analyst, apart from the known risks of loss in such a procedure. The wet-oxidation procedure described is suitable for the purpose. Prolonged digestion is necessary and decomposition products of the perchloric acid may give spuriously high diffusion currents for the copper wave. Such effects have been noted by other workers.[18]

APPARATUS—

A Tinsley pen-recording polarograph was used.

TABLE I

DETERMINATION OF COPPER IN GELATIN BY VARIOUS METHODS

Copper found by—				
2:2′-diquinolyl method, p.p.m.	bis*cyclo*hexanone oxalyldihydrazone method, p.p.m.	neocuproine method, p.p.m.	polarographic method, p.p.m.	zinc dibenzyldithiocarbamate method, p.p.m.
14·5	11·7	12·2	13·4	14·5
3·5	1·9	3·5	3·3	2·4
8·0	7·8	8·1	8·6	8·1
3·0	1·4	3·4	2·4	1·5
3·0	1·8	3·3	2·8	1·4
1·0	0·0	0·7	0·5	0·0
1·0	0·0	1·0	1·0	0·0

PROCEDURE—

After digestion, transfer the cooled solution to a 10-ml calibrated flask and dilute to the mark with distilled water. This solution, which is approximately 5 *N* in sulphuric acid,

is used directly for the polarographic determination. No maximum suppressor is required. It is convenient to use a mercury pool as anode; the half-wave potential of the copper wave is at −0·34 volt against the pool. Preliminary experiments showed that variations in sulphuric acid concentration from 3 to 8 *N* did not seriously affect the wave heights.

Results

The results by these four methods on seven commercial gelatins are shown in Table I. Figures obtained with the zinc dibenzyldithiocarbamate procedure of Andrus[19] with special precautions to minimise light fading are included for comparison.

In a series of recovery experiments, known amounts of copper were added to the gelatins before digestion. The average recoveries were as follows—

2:2′-Diquinolyl method	101 ± 5 per cent.
Bis*cyclo*hexanone oxalyldihydrazone method ..	96 ± 5 per cent.
Neocuproine method	99 ± 5 per cent.
Zinc dibenzyldithiocarbamate method	96 ± 5 per cent.

The results shown in Table I are reasonably satisfactory, considering the low concentrations involved and the simplicity of the instruments used for measuring.

Comparison of the Methods

Sensitivity—

Caution must be exercised in comparing sensitivities with filter instruments. According to the values given in the literature, zinc dibenzyldithiocarbamate[6] has about the same sensitivity as bis*cyclo*hexanone oxalyldihydrazone,[20] when both complexes are measured with a spectrophotometer. In this work, with the best filter available, the zinc reagent was only about one-third as sensitive. On the other hand, bis*cyclo*hexanone oxalyldihydrazone was found to be about 2½-times as sensitive as 2:2′-diquinolyl. This figure is in agreement with those of other workers.[20] However, this advantage is offset by the "concentrating" effect of the extraction stage in the latter case. Like other workers,[17] we have found 2:2′-diquinolyl and neocuproine to be very similar in sensitivity.

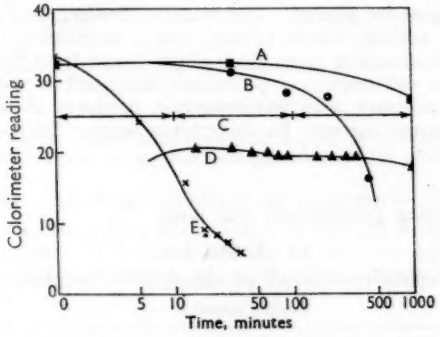

Fig. 2. Colour stability: curve A, sodium diethyldithiocarbamate in fluorescent light; curve B, sodium diethyldithiocarbamate in diffuse daylight; curve C, 2:2′-diquinolyl and neocuproine in all lighting: curve D, bis*cyclo*hexanone oxalyldihydrazone in all lighting; curve E, sodium diethyldithiocarbamate in sunlight

Interference—

The only known interference when the 2:2′-diquinolyl and neocuproine methods are used is from ferric iron, and this can be masked by tartaric acid. The zinc dibenzyldithiocarbamate method is affected by the presence of bismuth, cobalt and nickel, and the polarographic method may be affected by stannous tin. There is no known interference with the bis*cyclo*hexanone oxalyldihydrazone method.

STABILITY OF THE COMPLEX TO LIGHT—

The relative stabilities of the various complexes to light of different kinds are illustrated in Fig. 2 (note the logarithmic time scale). A curve is shown for sodium diethyldithiocarbamate; the zinc dibenzyldithiocarbamate reagent complex fades almost as quickly in bright light. As has been reported,[21] the bis*cyclo*hexanone oxalyldihydrazone complex fades slowly; this may be partly due to high salt concentration.[15] The 2:2′-diquinolyl and neocuproine complexes are stable to light for at least several days.

STABILITY OF THE REAGENT—

Carbamate-type reagents deteriorate on keeping.[22,23] 2:2′-Diquinolyl solution, when prepared as described, is stable for at least 3 months. Bis*cyclo*hexanone oxalyldihydrazone solution is less stable and becomes yellow after a few days. A freshly prepared solution of this reagent, with the addition of a standard amount of copper, gave a reading of 25·2 colorimeter units; when 4 days old, with the same amount of copper, it gave a reading of 20·6 units. The need to keep neocuproine solution in a refrigerator has been mentioned. When the solution was kept at laboratory temperature, the reading with a standard amount of copper fell from 25·7 units when fresh to 22·0 units at 4 days old.

PRICE OF THE REAGENT—

2:2′-Diquinolyl and neocuproine are fairly expensive reagents; by taking into account the difference in the concentrations used, they are about the same cost. Bis*cyclo*hexanone oxalyldihydrazone is about the same price as carbamate reagents.

CONCLUSIONS

2:2′-Diquinolyl and neocuproine are equivalent in most respects except for the stability of the reagent. The stabilities of the complexes to light favour these reagents; simplicity, sensitivity and economy favour bis*cyclo*hexanone oxalyldihydrazone. All these reagents have advantages over sodium diethyldithiocarbamate. The polarographic method is simple and convenient, although possibly not so generally attractive as a colorimetric method.

By taking into account all the above factors, the preferred reagent is 2:2′-diquinolyl. The procedure described, used in place of the British Standard method, has given satisfactory results during 6 months.

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The Spectrophotometric Determination of Gallium in Rocks and Minerals

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The use of a mixed solvent consisting of chlorobenzene containing 25 per cent. v/v of carbon tetrachloride is recommended for the photometric determination of gallium, since it extracts rhodamine B chlorogallate completely from 6·5 *N* hydrochloric acid; the presence of titanous chloride suppresses the reagent blank value. The procedure described has approximately three times the sensitivity of the rhodamine B method of Onishi and Sandell, who use benzene for the extraction. The determination of gallium in silicate, oxide, sulphide and carbonate minerals is described. U.S. Geological Survey standard rocks G1 and W1 were found to contain 21·3 and 21·5 p.p.m. of gallium (coefficients of variation ±1·3 and ±1·9 per cent., respectively).

It has been known for a long time that antimony, as Sb^{5+}, thallium, as Tl^{3+}, iron, as Fe^{3+}, and gold, as Au^{3+}, react with rhodamine B in hydrochloric acid medium to give red or violet complexes that are soluble in benzene. Recently, Onishi[1] has reported that gallium forms a similar complex. Onishi and Sandell[2] have extracted this complex with benzene for the photometric and fluorimetric determination of microgram amounts of gallium, after its separation from interfering elements by extraction from hydrochloric acid medium with di*iso*propyl ether.

Attempts to use this method in these laboratories led to very variable results for both blank values and determinations; the coefficient of variation was ±15 per cent. This variation was attributed to the difficulty of always attaining the same equilibrium point in the extraction, since less than half the rhodamine B chlorogallate complex is extracted into the benzene phase,[2] the ratio being as follows—

$$\frac{[Ga]_{C_6H_6}}{[Ga]_{H_2O}} = 0{\cdot}57.$$

The extraction is sensitive to variation in both hydrochloric acid and rhodamine B concentrations. Benzene has two further disadvantages, namely, its high toxicity and its low density, which makes it necessary to separate the aqueous phase before making photometric measurements.

Experimental

It was decided to test whether complete extraction of the rhodamine B chlorogallate complex could be achieved by using any solvent having a density greater than 1·10. Experiments were carried out by treating 5 ml of 6 *N* hydrochloric acid, both alone and in the presence of 5 μg of gallium, with 0·5 ml of a 0·5 per cent. solution of rhodamine B and 8 ml of the appropriate solvent. After the mixture had been shaken for 10 minutes, the organic phase was filtered through a glass-wool plug, 1 ml of ethanol was added and the solution was diluted to 10 ml with the solvent. The optical densities of the solutions were measured at 562 mμ in 1-cm cells. Further tests were made in the same manner with 5 ml of 6·5 *N* hydrochloric acid containing 1 per cent. of titanous chloride instead of the 6 *N* acid, since it was found that the presence of the titanous salt drastically reduced the reagent blank value and prevented any interference by traces of ferric iron. The results of these experiments are shown in Table I.

Organic solvents differ considerably in their ability to extract rhodamine B and its chlorogallate, and hence carbon tetrachloride extracts neither appreciably, whereas both are strongly extracted by chloroform. Chlorobenzene is intermediate in properties, but, owing to the similarity of its density to that of 6 *N* hydrochloric acid, it tends to form a rather stable emulsion. It is possible that the inclusion of a small amount of the aqueous phase accounts for the rather high optical densities recorded when this solvent is used.

TABLE I

EXTRACTION OF RHODAMINE B CHLOROGALLATE BY VARIOUS SOLVENTS

Solvent	Optical density, for tests in which 6 *N* hydrochloric acid was used, of—			Optical density, for tests in which 6·5 *N* hydrochloric acid containing 1 per cent. of titanous chloride was used, of—		
	blank	test containing 5 μg of gallium	Difference	blank	test containing 5 μg of gallium	Difference
Benzene	0·029	0·299	0·270	0·009	0·259	0·250
Chlorobenzene ..	0·334	1·104	0·770	0·034	0·734	0·700
Chloroform	5·90*	6·00*	0·10	5·80*	6·00*	0·20
Carbon tetrachloride..	0·007	0·007	0·000	—	—	—

* Solutions diluted before measurement and the values calculated for original concentration.

When the extraction was carried out with chlorobenzene containing 25 per cent. by volume of carbon tetrachloride, very rapid separation of the phases ensued. By using this solvent, greater than 99·5 per cent. extraction of the rhodamine B chlorogallate complex was achieved, hence giving effectively an approximately threefold increase in sensitivity compared with benzene. This mixed solvent was used in all subsequent work.

EFFECT OF VARIATION OF HYDROCHLORIC ACID CONCENTRATION ON THE EXTRACTION—

The effect of variation of the hydrochloric acid concentration of the aqueous phase was investigated by extracting five aliquots of various normalities of hydrochloric acid containing 1 per cent. of titanous chloride and 0·5 ml of a 0·5 per cent. solution of rhodamine B with 8 ml of a chlorobenzene - carbon tetrachloride mixture for 10 minutes. The organic phase was run through a plug of glass-wool into a 10-ml calibrated flask, 1 ml of ethanol was added and the liquid was diluted to volume with the solvent. The optical densities of the extracts were measured at 562 mμ in 1-cm cells. Similar extractions were made in the presence of 5 μg of gallium. The results, which are shown in Table II, indicate that the optimum acidity for the extractions lies in the range 6 to 6·5 *N*. For all later work, the hydrochloric acid concentration was standardised at 6·5 *N*.

TABLE II

EFFECT OF HYDROCHLORIC ACID CONCENTRATION ON THE EXTRACTION

Concentration of acid, *N*	4·0	5·0	6·0	6·5	7·0	8·0
Optical density of blank	0·093	0·029	0·015	0·011	0·009	0·007
Optical density of solution containing 5 μg of gallium	0·383	0·520	0·580	0·571	0·484	0·305
Optical-density difference	0·290	0·491	0·565	0·560	0·475	0·298

EFFECT OF VARIATION OF RHODAMINE B CONCENTRATION—

Since the concentration of rhodamine B exerts a marked effect on the efficiency of extraction of rhodamine B chlorogallate by benzene, its effect on the extraction with the chlorobenzene - carbon tetrachloride mixture was examined. The extractions were carried out as described for the variation of hydrochloric acid concentration, with the exception that the acid concentration was fixed at 6·5 *N* and the volume of 0·5 per cent. solution of rhodamine B was varied. Water was added to maintain the volume of the aqueous phase at 5·7 ml. The results, which are shown in Table III, indicate that complete extraction takes place when 0·5 to 0·7 ml of a 0·5 per cent. solution of rhodamine B is present.

TABLE III

EFFECT OF VARIATION OF RHODAMINE B CONCENTRATION

Volume of 0·5 per cent. rhodamine B solution present, ml ..	0·02	0·06	0·20	0·30	0·40	0·50	0·60	0·70
Optical density of blank	0·001	0·003	0·005	0·008	0·010	0·013	0·014	0·016
Optical density of solution containing 5 μg of gallium.. ..	0·171	0·358	0·469	0·519	0·551	0·576	0·578	0·585
Optical-density difference ..	0·170	0·355	0·464	0·511	0·541	0·563	0·564	0·569

USE OF TITANOUS CHLORIDE FOR SUPPRESSING THE REAGENT BLANK—

The presence of even small concentrations of titanous chloride in the aqueous phase reduces the reagent blank value by a factor of ten. In the presence of 0·001 per cent. of titanous chloride, a reagent blank value (optical density) of 0·015 was found, whereas when the extraction was carried out in the presence of 0·0005 per cent. of titanous chloride, or in its absence, a reagent blank value of 0·130 was found. These amounts of titanous chloride are well below the concentrations stoicheiometrically equivalent to the rhodamine B present. Its mode of action is at present obscure, but it may act by preventing oxidation of the dye itself to compounds soluble in the organic phase.

METHOD

All spectrophotometric measurements were made with a Unicam SP500 spectrophotometer at a slit width of 0·02 to 0·03 mm.

REAGENTS—

Hydrochloric acid, 6·5 N—Dilute 650 ml of concentrated hydrochloric acid, sp.gr. 1·16, to 1 litre.

Titanous chloride solution, 15 *per cent. w/v.*

Diisopropyl ether—Freshly distilled from sodium hydroxide.

Hydrochloric acid, about 6·5 N, *containing* 1 *per cent. of titanous chloride*—Mix 325 ml of concentrated hydrochloric acid with 33 ml of 15 per cent. w/v titanous chloride solution and dilute to 500 ml.

Rhodamine B solution—Dissolve 0·5 g of rhodamine B in 100 ml of water. Filter the solution before use.

Chlorobenzene - carbon tetrachloride mixture—Dilute 125 ml of carbon tetrachloride to 500 ml with monochlorobenzene.

Standard gallium solution, 5 *μg per ml*—Prepare a solution containing 0·4381 g of caesium gallium sulphate per litre, *i.e.*, 50 μg of gallium per ml. For use, dilute 10 ml of this solution to 100 ml.

PROCEDURE FOR DECOMPOSING THE SAMPLES—

Silicate minerals—Weigh 0·1 to 0·5 g of the finely ground sample (2·5 to 7·5 μg of gallium) in a platinum crucible, and add 1 ml of concentrated sulphuric acid and 15 ml of 40 per cent. hydrofluoric acid. Heat the covered crucible on a water bath overnight. Evaporate the hydrofluoric acid and then heat the crucible under an infra-red heater until copious white fumes are evolved. Dissolve the residue in 50 ml of 6·5 *N* hydrochloric acid. Determine gallium as described later.

Sulphide minerals—Evaporate to dryness a solution of 1 g of the powdered sample dissolved in 3 ml of bromine and 20 ml of a mixture of equal volumes of concentrated nitric and hydrochloric acids. Evaporate the residue to dryness again with 5 ml of concentrated hydrochloric acid. If arsenic or antimony is present in quantity, add 5 ml of 47 per cent. w/w hydrobromic acid and again evaporate to dryness. Dissolve the residue in 50 ml of 6·5 *N* hydrochloric acid; use the solution for the determination of gallium as described later.

Oxide minerals—Fuse 0·1 to 1 g of the oxide mineral (up to 10 μg of gallium) in a platinum crucible with ten times its weight of potassium pyrosulphate. Dissolve the cold melt in 50 ml of 6·5 *N* hydrochloric acid; determine gallium in the solution as described later.

Carbonate minerals—Dissolve 2 to 3 g of the mineral in dilute hydrochloric acid, filter if necessary, and add hydrochloric acid to bring the acidity to 6·5 *N*. Determine gallium as described later.

In each test, carry out a determination of the reagent blank in the same manner, but omitting the sample.

PROCEDURE FOR EXTRACTING GALLIUM WITH DI*iso*PROPYL ETHER—

Transfer the solution of the sample to a 250-ml separating funnel, add an excess of 15 per cent. w/v titanous chloride solution (5 ml is usually sufficient) and extract twice with equal volumes of di*iso*propyl ether. Evaporate the combined extracts in a 100-ml beaker on a water bath.

PROCEDURE FOR DETERMINING GALLIUM—

Add 5 ml of 6·5 *N* hydrochloric acid containing 1 per cent of titanous chloride to the beaker containing the dry residue from the ether extraction. Warm the covered beaker to 70° to 80° C to dissolve the residue. Transfer the cold solution to a 50-ml separating funnel containing 8 ml of the chlorobenzene - carbon tetrachloride mixture. Rinse the beaker with a further 1 ml of 6·5 *N* hydrochloric acid and add the washings to the funnel. Add 0·5 ml of rhodamine B solution and shake the separating funnel mechanically for 10 minutes. Set aside until the two phases have separated. Run off the organic layer through a plug of glass-wool into a 10-ml calibrated flask containing 1 ml of ethanol. Wash the aqueous phase with a further 1 ml of the solvent and add the washings to the calibrated flask. Dilute the solution to 10 ml with the solvent. Measure the optical density of the extract at 562 mμ in a 1-cm cell. Prepare a calibration curve by using 1, 2, 4, 6, 8 and 10 μg of gallium.

TEST OF THE METHOD

BEER'S LAW AND REPRODUCIBILITY—

Various amounts of gallium in 5-ml aliquots of 6·5 *N* hydrochloric acid were treated with rhodamine B solution and extracted as described above. The optical densities of the extracts, measured at 562 mμ in 1-cm cells, are given in Table IV. They show a satisfactory reproducibility and indicate that Beer's law is obeyed for up to at least 10 μg of gallium.

TABLE IV

PHOTOMETRIC DETERMINATION OF GALLIUM WITH RHODAMINE B

Weight of gallium, μg	2	4	6	8	10	
Optical density* measured at 562 mμ in a 1-cm cell	0·226, 0·230	0·450, 0·449	0·669, 0·674	0·907, 0·902, 0·897	1·140, 1·129, 1·121	
Mean optical density per μg of gallium	0·1140	0·1125	0·1120	0·1128	0·1130	Mean = 0·1129

* Less reagent blank of 0·012.

When the aqueous phases from the extraction of two samples, containing 5 and 10 μg of gallium, respectively, were re-extracted with the chlorobenzene - carbon tetrachloride mixture, the second extracts had the same optical density as the reagent blank. This indicated that complete extraction of the gallium had taken place in the first extraction. The molecular extinction coefficient of rhodamine B chlorogallate, calculated from the mean of the data in Table IV, is 78,900. This may be compared with the value of about 60,000 recorded by Onishi and Sandell,[2] when the extraction was carried out with benzene. The lowness of their coefficient is probably caused by the low percentage extraction found with benzene.

In order to test the accuracy and reproducibility of the proposed method for the analysis of silicates, five replicate analyses were made for gallium in the U.S. Geological Survey standard granite G1 and diabase W1. These rocks have been used in a collaborative test of methods for the determination of the major and minor components of silicate rocks.[3] Six determinations, mainly spectrographic, of gallium in G1 and W1 gave average figures of 17·5 and 14·5 p.p.m. of gallium, respectively. Not much reliance can be placed on these averages, since they are derived from figures having a rather large spread (15 to 20 p.p.m. for G1 and 11 to 20 p.p.m. for W1). In the present work, concentrations of 21·4, 21·7, 21·1, 21·3, 20·9, mean 21·3 p.p.m. of gallium and coefficient of variation ±1·3 per cent., and 21·5, 21·6, 20·9, 21·9, 21·8, mean 21·5 p.p.m. of gallium and coefficient of variation ±1·9 per cent. were found for G1 and W1, respectively. These results show a satisfactory precision and are in reasonable agreement with earlier work.

EFFECT OF INTERFERING ELEMENTS—

A study has been made of the possible interference, in the rhodamine B method, of a number of elements that are extracted by di*iso*propyl ether from 6·5 *N* hydrochloric acid solution. The solution of the element in 5 ml of 6·5 *N* hydrochloric acid containing 1 per cent. of titanous chloride was treated with 0·5 ml of 0·5 per cent. rhodamine B solution and extracted as described on p. 210. The results, which are shown in Table V, indicate that

appreciable interference is caused by antimony, as Sb^{3+}, arsenic, as As^{3+}, and thallium, as Tl^{+}. Of these elements, only antimony and arsenic are extracted by ether from a reducing medium. Ether extraction of solutions containing 10 mg of antimony, arsenic and thallium in the presence of titanous chloride, followed for the first two elements mentioned by evaporation with hydrobromic acid, gave no detectable colour in the rhodamine B method. The interference caused by thallous thallium in the rhodamine B method is rather surprising, since monovalent elements do not normally form extractable complexes with rhodamine B.

TABLE V

INTERFERENCE OF ELEMENTS EXTRACTABLE BY DI*iso*PROPYL ETHER

Element added	Amount added, μg	Optical density* measured in a 1-cm cell	Gallium equivalent of optical density, μg
Antimony	100 as Sb^{3+}	0·005	0·04
	10,000 as Sb^{3+}	0·258	2·3
Arsenic	100 as As^{3+}	0·004	0·04
	10,000 as As^{3+}	0·096	0·9
Germanium	100 as Ge^{4+}	0·000	0·00
Gold	100 as Au^{3+}	0·003	0·03
Indium	100 as In^{3+}	0·001	0·01
Iron	100 as Fe^{3+}	−0·002	−0·02
Molybdenum	100 as Mo^{6+}	−0·002	−0·02
Thallium	100 as Tl^{+}	0·120	1·1
Tin	100 as Sn^{2+}	0·000	0·00

* Reagent blank deducted.

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Differential Electrolytic Potentiometry

Part II.* Precision and Accuracy of Applications to Redox Titrimetry

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The precision and accuracy of differential electrolytic potentiometry applied to a random assortment of redox titrations have been examined. The accuracy compares well, even favourably, with classical potentiometry, and the precision, by virtue of the sharpness of the end-points, shows an improvement of 2 to 10-fold. The continuous flow of current appears to accelerate the attainment of equilibrium in electrode potentials by a similar factor. Investigation of the behaviour of individual electrodes under the influence of minute electrolytic currents has established that generally the anode anticipates or leads, and the cathode lags behind, the classical, or zero current, indicator electrode potential. The combination of lead and lag gives rise to titration curves that take the shape of the first differential of the classical potentiometric curve.

DIFFERENTIAL electrolytic potentiometry[1] is a titrimetric electrometric technique, in which the difference in potential between two electrodes, active or inert, at which electrolysis is proceeding under the influence of a minute heavily stabilised current, is measured during the process of titration, and it affords a method of investigating both total and partial reactions and of locating the end-point of the titration. The electrolysis current is less than the diffusion current of the electro-active species, and the solutions are normally stirred. The most fruitful investigational and developmental approach to the method is from the aspect of straightforward electrolysis.

* For details of Part I of this series, see reference list, p. 222.

The antecedents of the method have been examined.[1] Dutoit and von Weisse[2] may be credited with the original use of electrolysis in titrimetry, although their method and instrumentation were necessarily crude and their results of limited virtue. Since that time, little direct use appears to have been made of simple electrolysis of stirred solutions in titrimetry. The Foulk and Bawden dead-stop method[3] is, of course, electrolytic in some respect, but cannot strictly be denominated amperometric if this be understood to refer to diffusion current measurement in quiescent solutions. Recent years have seen the development of many techniques to which differential electrolytic potentiometry bears some relation, including derivative polarography,[4] constant and zero current potentiometry,[5] bimetallic[6] and differential metallic[7] systems, and so on. The present investigations have revealed that so-called constant current methods are misnamed in that the currents, no matter how heavily stabilised they may be, do vary; that methods involving passage of current through the standard half cell - indicator electrode circuit are inherently subject to errors, which may be significant; and that zero current methods, when construed as infinitesimal current methods in the usual practical meaning of the magnitude term, call for some care in the interpretation of their results.

Hitherto, attempts to explain the mechanism of such methods as the dead-stop have often leaned upon the term polarisation, a convenient word for concealing ignorance, though rather vague when pressed particularly and quantitatively. Defined as any process that tends to oppose or alter the flow of current at an electrode, polarisation can also be used to explain differential electrolytic potentiometry, but, since the current continues to flow with but little variation if stabilisation is adequate, it does not suffice to say that an electrode becomes conducting, or ceases to conduct, at a critical point in the chemical reaction. In the differential electrolytic potentiometric method, two factors are involved: first, an electrolysis current is passing through electrodes and solution, which will entail ohmic and decomposition potentials, and potentials arising from phenomena occurring during the passage of electrons through the layers on either side of the electrode - solution boundary; second, Nernstian potentials dependent on solution concentrations will arise. The electrodes exercise a dual function, in which indication is superimposed on electrolysis. These investigations offer some light on the broad question of electrode reactions, and further detail will be dealt with in a later paper, but for the moment a qualitative picture of how the different types of titration curve arise may suffice.

Examination of the behaviour of individual electrodes and comparison with the behaviour of a normal indicator electrode has shown that the electrodes behave quite independently of each other; that they tend, increasingly as the electrolysis current density diminishes, to follow the potential of the infinitesimal current (indicator) electrode, but either lag (cathode) or lead (anode); that the form of the differential electrolytic potentiometric curve depends on the reversibility of the species, not necessarily those of the over-all analytical reaction, being electrolysed at the two electrodes; and that the potentials are, in a measure, under the control of the operator.

In this paper, application of the method to electron-transfer reactions is reported, and among such reactions two main types of titration curve are found.

Type 1: reactions in which both oxidant and reductant are reversibly electrolysed—

In this instance the electrolysis anode potential (A in Fig. 1) leads, in terms of the volume or x-axis, the indicator electrode potential (B in Fig. 1), and the electrolysis cathode potential (C in Fig. 1) lags behind the indicator electrode potential. The amount of lag or lead is, in a measure, controllable by regulation of current density and ballast ratio. On the horizontal part of the potentiometric (indicator electrode) curve, between points P and Q in Fig. 1, the difference in potential between the two electrolysis electrodes is small; then, as the potentiometric curve turns upwards in the usual S-bend, between points Q and R, the x-axis lead of the anode in terms of y-axis potential increases, as also does the cathode lag, so that the potential difference between anode and cathode increases rapidly to the point of inflexion of the potentiometric curve. Thereafter, the slope of the potentiometric curve decreases between points R and S, and the anode lead and cathode lag in terms of y-axis potential fall until, when the potentiometric curve again becomes horizontal, between points S and T, the potential difference between anode and cathode again becomes small. The result is that the potential difference between electrolysis anode and cathode, initially small,

rises to a very sharp peak at the end-point and then falls to a low value again, giving, in effect, the first differential of the potentiometric curve, as shown at D in Fig. 1, the curve being moved along the x-axis for clarity. The smaller the lag and lead, the sharper is the peak. Potentiometric inflexion points do not necessarily coincide with reaction equivalence points, particularly in electronically unsymmetrical reactions.[3] It has several times been observed that the lag and lead of the electrolysis electrodes may be unsymmetrical, and the differential electrolytic potentiometric end-point then agrees with the equivalence point rather than with the potentiometric inflexion point, although the differences between these three points are usually minute in ordinary volumetric titrations. Further, certain reactions are over-all irreversible, as, for example, Mn^{II}/Mn^{VII}, but give the reversible type of curve. This may be ascribed to the fact that the electrolytically active species may not be those of the over-all analytical redox half reaction, and indeed may be present only in minute traces due to secondary, side or induced reactions, *e.g.*, in the above-mentioned example the active species may be Mn^{II}/Mn^{III}, but there are many possibilities involving oxidant, reductant or a combination thereof.

TYPE 2: REACTIONS IN WHICH EITHER OXIDANT OR REDUCTANT IS NOT REVERSIBLY ELECTROLYSED—

Here, one electrolysis electrode alone is operative, and behaves as in type 1, although the potential changes are greatly magnified, possibly because electrolytic and indicator effects are now entirely concentrated in one electrode. The other electrode takes up a fairly steady potential, which usually shows a small inflexion near the end-point. Ideally, if the half reaction is quite irreversible and none of the reaction products or intermediates is electrolysable at that electrode, then the potential taken up by the inactive electrode would be constant, and the differential curve would have the shape of a magnified potentiometric curve; it would, in fact, be that of the active electrode. When partial reversibility of reactant or other substance occurs, small inflexions appear on the inactive electrode, increasing with increasing reversibility and with diminishing electrolytic current density, and unsymmetrical curves, intermediate between the two types, result. It is convenient to partition this class into two sub-divisions, depending on which electrode is inactive, and, since the oxidant is more frequently added from the burette, they will be considered on this basis.

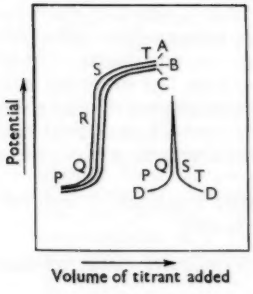


Fig. 1

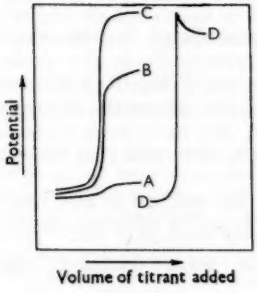


Fig. 2

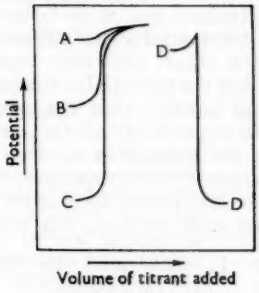


Fig. 3

Fig. 1. Reactions of type 1: curve A, anode potential; curve B, indicator electrode potential; curve C, cathode potential; curve D, differential electrolytic potentiometric curve

Fig. 2. Reactions of type 2(*a*): curve A, cathode potential; curve B, indicator electrode potential; curve C, anode potential; curve D, differential electrolytic potentiometric curve

Fig. 3. Reactions of type 2(*b*): curve A, anode potential; curve B, indicator electrode potential; curve C, cathode potential; curve D, differential electrolytic potentiometric curve

Type 2 (*a*) (*the oxidant not being reversibly electrolysable*)—In this instance the electrolysis cathode usually takes up a steady potential (A in Fig. 2), negative with respect to the indicator electrode potential (B in Fig. 2), whereas the anode (C in Fig. 2) follows the indicator electrode potential, but runs much more positive after the end-point. This should give an S-shaped differential curve, but in practice oxidation products of the reductant, or other substances present or formed, show some reaction at the cathode as shown in Fig. 2 and the result is a true differential curve, D, in which the potential, starting at a low value, rises to a peak at

the end-point, falls slightly and becomes steady. As reversibility of electrolysis of the oxidant increases and the electrolysis current density falls, the cathode curve shows a more pronounced inflexion, and the fall in potential after the end-point becomes greater, so that the curve tends more to the shape of type 1.

Type 2 (*b*) (*the reductant not being reversibly electrolysable*)—The anode, now inactive, attains a high potential with respect to the indicator electrode potential and either, ideally, remains steady or, as partial reversibility occurs and the anode current density decreases, shows an increasing upward inflexion (A in Fig. 3), joining and coinciding with the indicator electrode curve, B, after the end-point. The cathode meanwhile assumes a strongly negative potential, C, which, in passing through the end-point, rises to coincide again with the indicator electrode potential. Once more the potential across the electrolysis electrodes gives a true differential curve, D, the rate of fall often exceeding 100,000 mV per ml. Starting at a high potential value, the curve climbs to a small peak at the end-point and then drops abruptly to zero. The apellation "true differential curve" will appear justified when it is remembered that the shape of the potentiometric curve for an irreversible reductant is of the **Z - S** form when taken on low-impedance instruments.[9] As the reversibility of the reductant system increases, the curves again tend towards the type 1 shape, as in the bromate - thallium[1] reaction.

When the reductant is added from the burette, the curve forms are, of course, transposed.

In general, the current, no matter how heavily ballasted, shows a small inflexion in reactions of type 1, in which both reactants are reversibly electrolysed, and this inflexion often coincides with the end-point. Some examples are shown in the later diagrams. When one reactant is irreversible, by using sufficiently small current densities, or by using very heavy ballasting, current variations can be suppressed at least below the sensitivity of the measuring instruments so far used. With lower ballasting, or higher current densities, variations in current occur, which can either be in the form of inflexions coinciding with the end-point, or be quite irregular.

Since the differential peaks may exceed 1000 mV, with slopes in excess of 100,000 mV per ml—indeed, on the ultra-micro scale, slopes over 10^8 volts per ml have been recorded[1]—the method is very sensitive, and, as the continuous flow of current appears greatly to accelerate the attainment of electrode potential equilibrium, straightforward titration, with a pH meter as indicator until the movement of potential suddenly reverses in direction, gives very precise results as quickly as titrations with visual indicators, although some of the peaks are so sharp in type 1 reactions (less than one drop of reagent) that care must be taken not to pass right through without observing them. In such instances the peak can be broadened to give warning of the end-point by appropriate control of conditions. The results here reported were found by the graphical method as a detailed survey of behaviour in the end-point region was desired. The method offers a precision of location of end-point better than classical potentiometry by a factor of 2 to 10, and the increased speed in attaining electrode potential equilibrium is of the same magnitude.

This paper deals with the investigation of the precision and accuracy of the method as applied to a random assortment of redox titrations, and of the behaviour of the individual electrodes in various chemical systems. Detailed examination of the variants of the method itself will be reported in a further paper; the application to the ultra-micro scale has already been covered.[1]

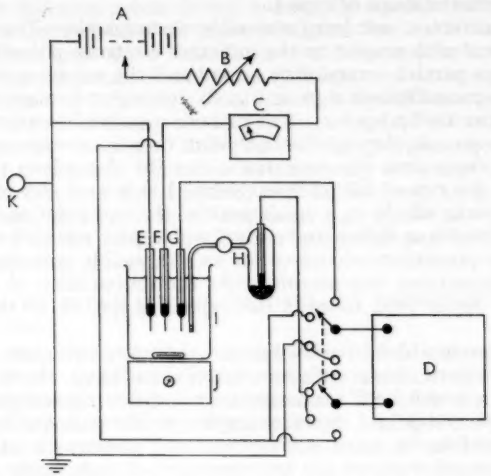
Method

Apparatus—

For routine titrations a very simple circuit is entirely satisfactory; all that is necessary are two platinum-wire electrodes immersed in the titration solution, and connected through a series (ballast) resistor to a battery. The potential is then measured across the two electrodes by means of a pH meter. As a general guide, the ballast resistor should not be less than 100 megohms, and the battery should be such as to give a current less than 1 microampere; although currents up to 6 microamperes and ballast resistors as low as 10 megohms can give satisfactory results. A resistance of 200 megohms and a battery of 2 to 120 volts will give excellent service.

The more elaborate circuit in Fig. 4 was used in this investigation to provide facilities for studying the behaviour of individual electrodes and for measuring currents.

Glassware, etc.—Volumetric glassware of NPL Grade A standard was check calibrated. Balances of sensitivities 5 μg at 50 g and 0·1 mg at 2 Kg were used with specially calibrated stainless-steel weights.



A = 0 to 1200-volt battery
B = 0 to 1000-megohm ballast resistors
C = 0 to 12-μA microammeter (Sangamo Weston S82)
D = pH meter. Special version of Doran model M 4981 fitted with four switched inputs of impedance 3×10^{12} ohms, and polarity reversing switch. By operation of the input switch, readings can be made of the potentials of—
(a) indicator electrode - calomel cell;
(b) electrolysis anode - calomel cell;
(c) electrolysis cathode - calomel cell;
(d) electrolysis anode - electrolysis cathode
E = Electrolysis cathode } 1 inch of 22 s.w.g. bright platinum wire sealed in glass
F = Electrolysis anode
G = Indicator electrode
H = Saturated calomel - potassium sulphate half cell, with saturated potassium sulphate salt bridge (potential 465 millivolts positive to normal hydrogen electrode)
I = Titration vessel, normally a 400-ml beaker (burette not shown)
J = Magnetic stirrer (magnet sealed in glass, speed controlled by Variac autotransformer)
K = Separate earth connection for negative pole of battery and all iron ware

Fig. 4. Circuit diagram

REAGENTS—

AnalaR reagents were used and were tested for the presence of active impurities. Quantitative reagents were prepared by purification of AnalaR chemicals, checked for purity by the recognised tests,[10] and assayed by potentiometric weight titrations. Solutions of these were prepared by direct weighing. Reagents such as cerium compounds, sodium thiosulphate, potassium antimonyl tartrate, not of ultimate standard quality, were checked by weight titrimetry in solution against ultimate standards.

PROCEDURE FOR PERFORMING THE TITRATIONS—

With a pipette, an aliquot of titrand is placed in the beaker, suitable amounts of acids and other reagents added to give the required concentrations at the end-point, and the solution diluted to give an end-point volume of 200 ml, due allowance being made for washings. The titrant is then added slowly from the burette with stirring until about 1 ml before the end-point, and the potentials allowed to settle down. Then diminishing increments of titrant are added, proceeding through the end-point in split drops, achieved by allowing a drop partially to form on the burette jet, picking it off with a glass rod, and washing it into the beaker, then increasing increments to at least 1 ml past the end-point. After

each increment, potentials are measured by switching the inputs of the meter in the order (*i*) indicator electrode - calomel, (*ii*) electrolysis anode - calomel, (*iii*) electrolysis cathode - calomel, and (*iv*) electrolysis differential potential. These are read at 2, 3 or 5-minute intervals (measured with a stopwatch), depending on the nature of the reaction, until the potential drift becomes less than 1 mV per minute. It is sometimes necessary to hold potentials in circuit for some time to allow capacitor charging currents to vanish. When high impedance circuits are being used, screening is necessary, and hand capacitance effects are encountered on handling the controls.

TABLE I

REACTIONS OF TYPE 1

Mean electrolysis current, μA	Theoretical consumption of titrant, ml	Consumption of titrant at— potentiometric inflexion point, ml	anode potential inflexion point, ml	cathode potential inflexion point, ml	differential peak, ml	current inflexion, ml
Titration of 0·1 M *ferrous iron with* 0·1 M *cerate, in* 0·5 M *sulphuric acid*—						
1·80	19·47	19·47	19·47	19·55	19·47	—
1·80		19·46	19·45	19·53	19·47	—
1·78		19·47	19·46	19·54	19·48	—
1·80	30·10	30·08	30·07	30·12	30·10	—
1·77		30·10	30·10	30·16	30·11	—
1·79		30·09	30·08	30·18	30·11	—
1·80	5·06	5·05	5·04	5·06	5·06	—
1·72		5·05	5·05	5·07	5·06	—
1·76		5·06	5·04	5·08	5·07	—
Titration of 0·1 M *ferrous iron with* 0·02 M *potassium permanganate, in* 0·5 M *sulphuric acid*—						
1·75	20·95	20·95	20·89	20·98	20·95	20·94
1·76		20·96	20·92	20·98	20·95	20·95
1·76		20·94	20·87	20·97	20·94	20·94
1·86	46·44	46·42	46·38	46·45	46·44	46·42
1·88		46·41	46·36	46·46	46·44	46·47
1·88		46·43	46·40	46·46	46·44	46·41
1·78	5·32	5·32	5·31	5·33	5·32	5·31
1·78		5·33	5·31	5·34	5·33	5·34
1·80		5·32	5·31	5·33	5·32	5·33
Titration of 0·1 M *ferrocyanide with* 0·1 M *cerate, in* 0·625 M *sulphuric acid*—						
1·77	25·80	25·80	25·80	25·81	25·80	25·90
1·80		25·81	25·80	25·82	25·80	25·88
1·82		25·81	25·80	25·81	25·80	25·86
1·90	10·31	10·30	10·30	10·31	10·31	10·38
1·91		10·31	10·30	10·32	10·30	10·36
1·86		10·31	10·30	10·32	10·31	10·35
Titration of 0·05 M *thallium*[1] *with* 0·01667 M *bromate, in* 1·0 M *hydrochloric acid*—						
1·86	24·43	24·44	24·40	24·47	24·43	24·43
1·89	24·42	24·42	24·38	24·46	24·43	24·42
1·88	24·43	24·43	24·38	24·46	24·43	24·43
2·00	25·63	25·62	25·58	25·68	25·63	25·62
1·98		25·62	25·56	25·66	25·63	25·62
1·88		25·65	25·57	25·69	25·64	25·64

The particular determinations recorded in this paper were made at an early stage in the work before all the factors had been investigated, and used rather high current densities. Some of the conditions are definitely sub-optimum, but this did not affect the point at issue, *viz.*, the accuracy of the analytical results. In most experiments a source potential of 600 volts with a ballast resistor of 300 to 350 megohms, and a pair of 1-inch 22-s.w.g. platinum-wire electrodes placed parallel and 1 inch apart were used. In this work, readings of current were taken at each increment of titrant. Where no entry is made in the current column in the results, no sharp inflexion was recorded.

RESULTS

REACTIONS OF TYPE 1—

Examples of reactions in which both oxidant and reductant are reversibly electrolysed include cerate - ferrous iron and permanganate - ferrous iron. Reactions in which one

reactant is only partly electrolysable, but in which the curves resemble the doubly reversible type rather than the singly reversible include cerate - ferrocyanide and bromate - thallium[I].

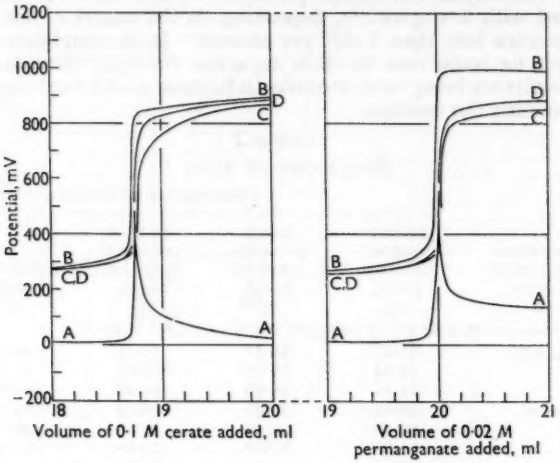


Fig. 5 Fig. 6

Figs. 5 and 6. Reactions of type 1: curve A, differential electrolytic potentiometry circuit; curve B, electrolysis anode - calomel cell circuit; curve C, electrolysis cathode - calomel cell circuit; curve D, indicator electrode - calomel cell circuit

Fig. 5. Titration of 0·1 *M* ferrous iron with 0·1 *M* cerate, in 0·5 *M* sulphuric acid

Fig. 6. Titration of 0·1 *M* ferrous iron with 0·02 *M* permanganate, in 0·5 *M* sulphuric acid

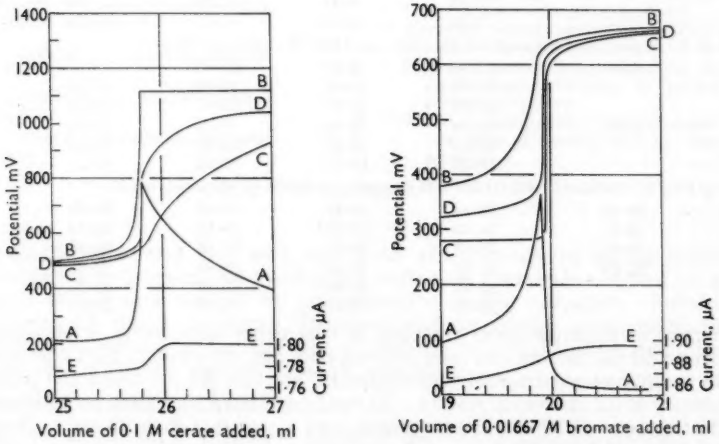


Fig. 7 Fig. 8

Figs. 7 and 8. Reactions approximating to type 1: curves lettered as for Figs. 5 and 6, except that curve E is the electrolysis current variation

Fig. 7. Titration of 0·1 *M* ferrocyanide with 0·1 *M* cerate, in 0·625 *M* sulphuric acid

Fig. 8. Titration of 0·05 *M* thallium[I] with 0·01667 *M* bromate, in 1·0 *M* hydrochloric acid

Titrations were carried out under conditions used in normal analytical practice. Results are given in Table I, and one example of the family of curves for each reaction is given in Figs. 5 to 8.

REACTIONS OF TYPE 2—

An example of type 2 (*a*), in which the oxidant is not reversibly electrolysed, is afforded by the dichromate - ferrous iron reaction. When the reductant is contained in the burette, curves of the same shape (potential rising from a low value to a sudden peak and then levelling off) are given by reactions in which the reductant is not reversibly oxidised, as in titrations of iodine with arsenic^{III}, antimony^{III} or thiosulphate. The rather anomalous case of the vanadate - ferrous iron reaction at such current densities bears some relation to type 2 (*a*) (unreversible oxidant, inactive cathode), and is therefore included in this class, but in this case an S-shaped curve is produced in which the end-point is the point of inflexion as in classical potentiometric curves.

TABLE IIA

REACTIONS OF TYPE 2 (*a*)

Mean electrolysis current, μA	Theoretical consumption of titrant, ml	Consumption of titrant at— potentiometric inflexion point, ml	anode potential inflexion point, ml	cathode potential inflexion point, ml	differential peak, ml	current inflexion, ml
Titration of 0·1 M *ferrous iron with* 0·01667 M *dichromate, in* 0·625 M *sulphuric acid*—						
1·71	20·86	20·86	20·85	20·88	20·88	—
1·82		20·86	20·85	20·86	20·87	—
1·79		20·84	20·84	20·88	20·87	—
Titration as above, with the addition of 0·8 M *phosphoric acid*—						
1·77	20·86	20·85	20·83	20·87	20·86	—
1·78		20·86	20·85	20·88	20·87	—
1·82		20·85	20·84	20·88	20·87	—
Titration of 0·1 M *vanadate with* 0·1 M *ferrous iron, in* 0·5 M *sulphuric acid*—						
1·72	29·63	29·64	29·65	29·6	29·65	29·25
1·72		29·62	29·64	29·6	29·66	29·30
1·74		29·64	29·66	29·6	29·66	29·25
Titration of 0·1 M *ferrous iron with* 0·1 M *vanadate, in* 0·5 M *sulphuric acid and* 0·8 M *phosphoric acid*—						
1·83	20·84	20·84	20·76	20·92	20·83	—
1·82		20·82	20·77	20·90	20·83	—
1·84		20·83	20·77	20·92	20·84	—
1·80	19·95	19·95	19·94	19·92	19·95	—
1·81		19·93	19·93	19·95	19·96	—
1·76		19·95	19·93	19·93	19·95	—
Titration of 0·1 M *iodine with* 0·05 M *arsenic*^{III}, *in bicarbonate buffer*—						
1·70	25·76	25·76	25·77	25·76	25·76	—
1·70		25·76	25·77	25·76	25·76	—
1·75		25·76	25·77	25·76	25·76	—
1·70		25·76	25·76	25·76	25·76	—
Titration of 0·1 M *iodine with* 0·05 M *antimony*^{III}, *in bicarbonate buffer*—						
1·70	25·40	25·40	25·39	25·40	25·40	—
1·70		25·39	25·39	25·40	25·40	—
1·70		25·40	25·40	25·40	25·40	—
Titration of 0·1 M *iodine with* 0·1 M *thiosulphate, in* 1·0 M *hydrochloric acid*—						
1·71	25·82	25·82	25·83	25·82	25·82	—
1·70		25·83	25·83	25·83	25·83	—
1·70		25·82	25·83	25·82	25·82	—
Titration of 0·1 M *copper*^{II}, *after addition of excess of iodide, with thiosulphate, in* 1·0 M *acetic acid*—						
1·71	24·67	24·67	24·69	24·66	24·67	24·65
1·72		24·66	24·68	24·66	24·67	24·65
1·72		24·67	24·68	24·67	24·67	24·65

TABLE IIB

REACTIONS OF TYPE 2 (*b*)

Mean electrolysis current, μA	Theoretical consumption, of titrant, ml	Consumption of titrant at— potentiometric inflexion point, ml	anode potential inflexion point, ml	cathode potential inflexion point, ml	differential peak, ml
Titration of 0·025 M *hydrazine with* 0·01667 M *bromate, in* 1·0 M *hydrochloric acid and* 0·1 M *potassium bromide*—					
1·80	24·79	24·79	24·80	24·79	24·79
1·80		24·79	24·79	24·79	24·79
1·80		24·79	24·80	24·79	24·79
1·79	5·00	5·00	5·01	5·00	5·00
1·79		5·00	5·00	5·00	5·00
1·79		5·00	5·00	5·00	5·00
Titration of 0·05 M *arsenic*^{III} *with* 0·01667 M *bromate, in* 1·0 M *hydrochloric acid*—					
1·79	25·21	25·21	25·22	25·21	25·21
1·80		25·20	25·21	25·21	25·21
1·79		25·21	25·21	25·21	25·21
Titration of 0·05 M *antimony*^{III} *with* 0·01667 M *bromate, in* 1·0 M *hydrochloric acid and* 0·1 M *potassium bromide*—					
1·80	25·60	25·60	25·60	25·60	25·60
1·80		25·61	25·60	25·60	25·60
1·80		25·60	25·60	25·60	25·60
Titration of 0·05 M *arsenic*^{III} *with* 0·05 M *chloramine-T:*					
(*a*) *in* 2·0 M *hydrochloric acid*—					
1·00	25·11	25·11	25·2	25·10	25·10
(*b*) *in* 2·0 M *hydrochloric acid and* 0·1 M *potassium bromide*—					
1·00	25·11	25·11	25·11	25·11	25·11
(*c*) *in bicarbonate buffer and* 0·005 M *potassium iodide*—					
1·00	25·11	25·12	25·11	25·11	25·11
(*d*)* *in* 4·0 M *hydrochloric acid, with the addition of* 2 *ml of* 1·0 M *iodine monochloride* (*Andrews-type titration*)—					
1·00	25·11	25·10	25·06	25·12	25·10

* The curve form is of type 1.

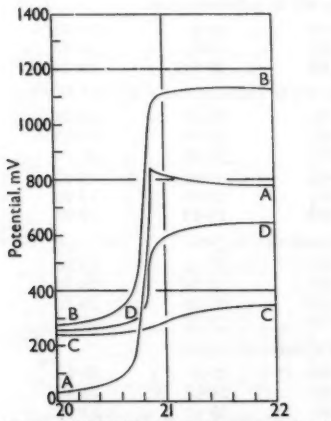


Fig. 9

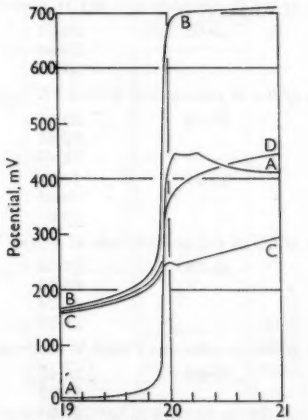


Fig. 10

Figs. 9 and 10. Reactions of type 2 (*a*): curves lettered as for Figs. 5 and 6

Fig. 9. Titration of 0·1 *M* ferrous iron with 0·01667 *M* dichromate, in 0·625 *M* sulphuric acid

Fig. 10. Titration of 0·1 *M* ferrous iron with 0·1 *M* vanadate, in 0·5 *M* sulphuric acid and 0·8 *M* phosphoric acid

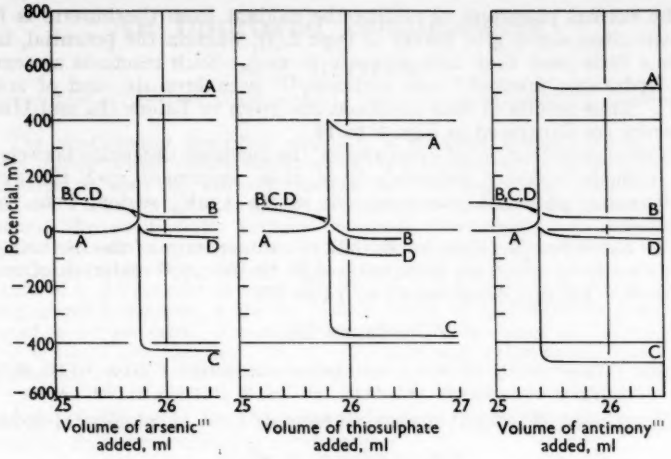


Fig. 11 Fig. 12 Fig. 13

Figs. 11, 12 and 13. Reactions of type 2 (*b*), in which reductant is added from the burette, giving curves of type 2 (*a*): curves lettered as for Figs. 5 and 6

Fig. 11. Titration of 0·1 *M* iodine with 0·05 *M* arsenic^{III}, in bicarbonate buffer solution

Fig. 12. Titration of 0·1 *M* iodine with 0·1 *M* thiosulphate, in 1·0 *M* hydrochloric acid

Fig. 13. Titration of 0·1 *M* iodine with 0·5 *M* antimony^{III}, in bicarbonate buffer solution

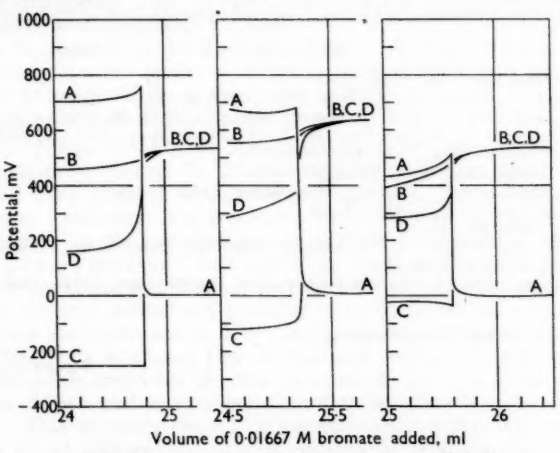


Fig. 14 Fig. 15 Fig. 16

Figs. 14, 15 and 16. Reactions of type 2 (*b*): curves lettered as for Figs. 5 and 6.

Fig. 14. Titration of 0·025 *M* hydrazine with 0·01667 *M* bromate, in 1·0 *M* hydrochloric acid and 0·1 *M* potassium bromide

Fig. 15. Titration of 0·05 *M* arsenic^{III} with 0·01667 *M* bromate, in 1·0 *M* hydrochloric acid

Fig. 16. Titration of 0·05 *M* antimony^{III} with 0·01667 *M* bromate, in 1·0 *M* hydrochloric acid and 0·1 *M* potassium bromide

When the normal procedure of adding the oxidant from the burette is followed, the iodine reactions cited above give curves of type 2 (*b*), wherein the potential, initially high, often rises to a little peak then falls abruptly to zero. Such reactions are exemplified by titrations of hydrazine, arsenic^{III} and antimony^{III} with bromate, and of arsenic^{III} with chloramine-T. Some results of such titrations are given in Tables IIA and IIB and typical families of curves are illustrated in Figs. 9 to 14.

It is worthy of note that, in all experiments, the algebraic difference between the anode - calomel and cathode - calomel potentials is in close agreement with the experimentally measured differential potential, commonly to within 1 mV; seldom does the difference exceed 2 mV.

Further, to check the precision (replicability) and accuracy of the method, some determinations were made by arbitrary standard weight titrimetry,[11] materials of atomic-weight purity being used. The results are shown in Table III.

TABLE III

WEIGHT TITRATION OF OXYGEN-SUBLIMED ARSENIOUS OXIDE WITH HIGHLY PURIFIED POTASSIUM BROMATE, IN 1·0 M HYDROCHLORIC ACID

Mean current, 0·795 μA; theoretical formula ratio of solutions, 1·00220

	Ratio of solutions by weight		
Potentiometric	Anode	Cathode	Differential
1·0021	1·002	1·00218	1·00219
1·0022	1·002	1·00217	1·00218
1·0022	1·002	1·00218	1·00220
1·0021	1·002	1·00220	1·00221
1·0021	1·002	1·00219	1·00220
1·0021	1·002	1·00218	1·00219

I thank Dr. V. J. Jennings, who contributed the work on the chloramine-T - arsenic^{III} reaction, and Imperial Chemical Industries Limited and the Baker Platinum Division of Engelhard Industries Limited for the loan of instruments and apparatus used in the work.

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NOTE—Reference 1 is to Part I of this series.

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An Improved Ebulliometer

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The ebulliometer described embodies a modified Cottrell pump and boiling cavity, which reduce superheating to a minimum. A suitably aged thermistor is used to measure temperature changes. The temperature variation of a boiling solution can be kept within $\pm$ 0·001° C for considerable periods. The ebulliometer permits the rapid determination of molecular weights. Results are presented for a wide variety of compounds with molecular weights from 100 to 314, determined in acetone or benzene. An error of $\pm$ 2·1 per cent. is obtained with 50-mg samples, each determination taking about 3 minutes; a 200-mg sample added in four portions gives an error of $\pm$ 0·8 per cent. The principles on which the design of the ebulliometer is based are discussed. It is noted that pure solvents are prone to superheating cycles, which are suppressed by adding small amounts of solute.

THE design of an ebulliometer for the accurate measurement of boiling-point differences should, if possible, fulfil the following conditions—

(*i*) The concentration of the solution, the temperature of which is being measured, should be constant and relatively insensitive to different rates of boiling.

(*ii*) There should be no residual superheating of the solution that is in contact with the thermometric element.

(*iii*) The temperature measured must be that of the solution in equilibrium with vapour at the boiling-point of the pure solvent.

(*iv*) If the thermometer is not to be immersed in the liquid, its heat capacity should be small, so that it can attain the temperature of the small volume of liquid with which it is in contact.

(*v*) The apparatus should come to equilibrium rapidly or appreciable errors can result from changes in atmospheric pressure.[1]

(*vi*) It should be possible to detect small changes of temperature accurately, so that measurements can be made in solutions sufficiently dilute for departures from ideality to be small for as many solutes as possible.

(*vii*) The apparatus should be reasonably simple to use.

In order to satisfy the first of these conditions, both the "dead space" and the internal surface of the ebulliometer should be small compared with the volume of the solution. Condensation should take place in a well defined region in the condenser and, so far as possible, nowhere else. Moreover, the condenser surface should be the smallest compatible with efficient working. In the conventional type of ebulliometer, which makes use of a Cottrell pump, the jets are positioned well above the liquid level and are protected from condensate by a sleeve enclosing the thermometer and the jets. This arrangement not only creates an excessive amount of dead space, but also entraps a certain amount of air. Hence the liquid that bathes the thermometer is not in equilibrium with saturated vapour. Some improvement is effected by wrapping the thermometer bulb with cotton-wool or muslin.[2,3] Although this considerably improves the steadiness of the readings, there is still a tendency to drift, and cycles of high and low temperature that fluctuate occasionally by as much as 0·01° C can occur. This is partly caused by condensation on the thermometer stem from colder parts of the vessel. Unless the rate of pumping is high, the thermometer cannot be maintained at a steady temperature, and the normal apparatus requires a long time to come to equilibrium.

The requirements of small dead space, high pumping speed and small condenser surface are incompatible with the usual designs of ebulliometer. Moreover, high pumping speeds mean that the work of pumping is appreciable and this has led to cycles of superheating. The liquid is often forced up the narrow tubes leading to the jets under sufficient pressure and at such velocities that it has not had time to dissipate its excess heat, although it is intimately mixed with vapour.[1] Gentle boiling and a short pump provide the best compromise.

Simple immersion of the thermometer in the boiling liquid is unsatisfactory for reasons that are not always clear, the most important being that the turbulence in the neighbourhood

of the thermometer bulb is never great enough to mix the liquid and vapour adequately. The temperature of the solution is not uniform throughout its bulk, as regions of superheating near the heat source grade to regions below the boiling-point at the surface of the container.[4] Hence, some arrangement has to be provided whereby an intimate froth of solution and vapour is brought into contact with the thermometer, preferably as near the liquid surface as possible.[5] This contact should also take place in a region that is completely saturated with vapour at the boiling-point and protected from condensate.

In the proposed apparatus the requirement of a thermometer with a small heat capacity is satisfactorily fulfilled by the use of a thermistor, and this has also made possible the design of an ebulliometer that approximately fulfils the other conditions previously stated.

The method of heating used with an ebulliometer is of great importance. The area over which heat is applied must be as small as possible if superheating is to be avoided. It has been shown[6] that there is a characteristic temperature difference between the heating surface and the liquid, of the order of 50° C for most liquids, for which heat transfer and hence ebullition is most efficient. This is the temperature region in which bubbles of vapour are formed at definite points on the heating surface; the remaining areas on the hot surface simply produce superheated liquid. Once it has left the surface, superheated liquid can only come into equilibrium by contact with vapour, or by heating the surrounding liquid, which is a slow process. Thus, by keeping the area of heat transfer small, a concentrated froth of vapour bubbles is produced, together with a relatively small amount of superheated liquid that does not penetrate far into the bulk of the liquid. Moreover, if the site of ebullition is isolated from the main body of the liquid the superheating is further minimised. In the proposed design, heat is supplied by a microburner and transferred by way of a platinum or tungsten wire sealed through the base of the vessel; a practice common to many ebulliometers.

Experimental

Tests were carried out on several Cottrell pumps with different tube diameters. It was noticed that for a given internal diameter the efficiency of pumping varied markedly with different solvents. A diameter of 2 mm, although adequate for acetone, was useless for water, and gave poor results with ethanol. A diameter of 3 mm allowed an adequate flow of ethanol, but, unless the length of tube above the liquid level was short, the pumping of water was unsteady. A minimum bore of 4 mm was needed for steady pumping with all three solvents.

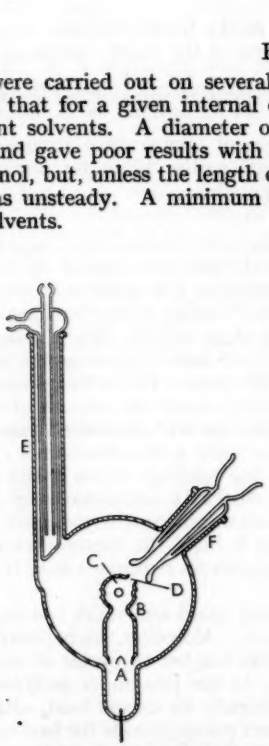

Fig. 1. Diagram of ebulliometer

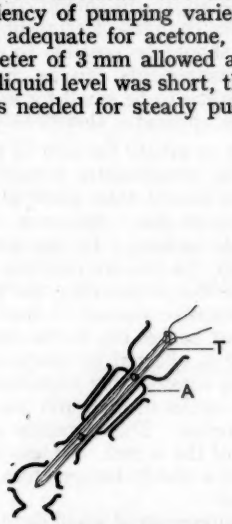

Fig. 2. Diagram showing position of thermistor

APPARATUS—

A diagram of the ebulliometer is shown in Fig. 1. The apparatus consists of a spherical flask approximately 5 cm in diameter. The boiling chamber, A, is in the shape of a tube that penetrates the flask and communicates with the bulk of the liquid by four holes just at the inner side of the junction with the flask. The tube extends about 2 cm below the flask and continues about 1·5 cm into the flask. The internal diameter of the tube is constricted from about 12 mm to approximately 4 mm at B. The constriction opens into a spherical cavity, C, 12 mm in diameter, pierced around its equator by four small holes, and with a fifth hole, D, just large enough to admit the thermistor at about 60° off the axis. A cold-finger condenser fits in the vertical tube, E, which has an internal diameter of about 1 cm. The thermistor is introduced through the standard B14 ground-glass socket, F.

The thermistor, T, fits into the tube in the ground-glass stopper, A (see Fig. 2). It is held in place by a rubber ring at the outer end of the tube and a polythene seal at the inner end, which is slightly flared for the purpose. This seal, which is effective for ethanol, water and acetone, is produced by melting the end of a stick of polythene and wrapping the semi-molten polythene round the thermistor just above the flare. While it is still soft, the polythene is forced into the annular space between the thermistor and the tube by means of a second glass tube slipped over its end. Later, a nylon sleeve was found to be of more general use. The tip of the thermistor should be at the centre of the cavity.[7]

The thermistor used was the design (series F) produced by Standard Telephones & Cables Ltd. It consists of a glass tube approximately 4 mm in diameter and 7 cm long. Through one end of the tube are sealed two copper leads that reach to about 1 cm from the tip and are separated by glass spacers. They are connected by very fine wire to a small mass of semi-conductor sealed into the glass at the tip.

The relationship between temperature, T, and resistance, R, for a thermistor[8] is approximately logarithmic, and is given by the equation—

$$\log R = \text{Constant} - bT$$

The constant and b differ for each thermistor, and the constant, which fixes the zero of the instrument, is liable to unpredictable fluctuations when the thermistor is new. Ageing, by repeatedly heating and cooling over the temperature range in which it is to be used, reduces these variations considerably. An alternative method of ageing, which can be applied to thermistors of high room-temperature resistance, *i.e.*, about 100,000 ohms, is to connect the thermistor to a 6-volt source at room temperature for 4 or 5 hours. Although it is not possible to measure absolute temperatures with greater accuracy than $\pm 0{\cdot}1°$ C, small changes in temperature can be determined with considerable precision. Moreover, when the temperature difference is of the order of 0·5° C, it is found that the relationship between the concentration of a boiling solution and the resistance of a thermistor in contact with it is sensibly linear. The thermistors used were of the type with a room-temperature resistance of about 100,000 ohms. These have a temperature coefficient of resistance of approximately −4·0 per cent. per °C.

The temperature coefficient of resistance was found to be constant. Examples of the sensitivity in ohms per °C of three thermistors at the boiling-point of acetone were as follows—

Thermistor	A	B	C
Approximate resistance at 56° C, ohms ..	32,000	33,000	22,500
Sensitivity at 56° C, ohms per °C ..	1207	1129	927

The advantages of the thermistor are—

(*i*) The minute heat capacity of its thermal element.
(*ii*) Its almost instantaneous response to even very small changes in the temperature of its environment.
(*iii*) Its resistance changes are large and a simple bridge circuit is adequate for their measurement.

The principal disadvantage is that each thermistor has to be aged and calibrated separately, but this can be overcome by calibrating the apparatus and thermistor as a whole for each solvent. This is done by determining changes of resistance for given concentrations of a standard substance in an optimum volume of solvent.

The resistance changes are measured by making the thermistor one arm of a Wheatstone bridge, the variable resistance of which is of the decade type with five decades.* A galvanometer with about 50 ohms internal resistance and a sensitivity of about 2 cm per μA is adequate to detect the out-of-balance current. The current actually passing through the thermistor should not exceed 0·2 mA.

The volume of solvent used should be sufficient to bring the liquid level a little way below the constriction in the boiling chamber. Models with capacities of 10, 20 and 25 ml have been used. These were optimum capacities, and with each there was a latitude of 5 ml either way.

The ebulliometer was originally designed to follow rates of reaction[9] and often the largest capacity was most useful for this purpose. For molecular-weight determinations, when only a small sample may be available, the smaller models are more suitable.

A draught shield is essential to obtain steady conditions.[4] This can conveniently be an asbestos cylinder that encloses both the ebulliometer and the microburner, as shown in Fig. 3. The boiling chamber projects through a hole in an asbestos sheet so that it is the only portion of the apparatus to be heated directly by the burner.

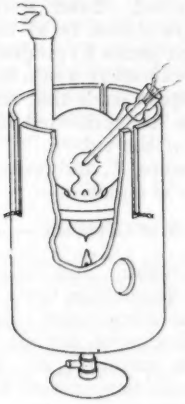

Fig. 3. Assembled apparatus with draught screen in position

When ebullition has commenced the central cavity is filled with a froth of vapour and liquid. The excess squirts through the equatorial holes and flows more gently outwards round the point of entry of the thermistor. This outward flow of liquid effectively keeps condensate away from the thermistor tip. Steady pumping can be maintained with very small flame heights. However, the temperature in the cavity is insensitive to difference in flame height, which can vary from less than $\frac{1}{4}$ to 1 inch.

It has been noted on many occasions that pure solvents have a greater tendency towards superheating and random fluctuations of temperature than have solutions containing very small amounts of solute. Once this small concentration of solute has been attained the temperature of the boiling liquid does not vary by more than 0·001° C for considerable periods; a condition that rarely occurs with a pure solvent. The first addition of solute to the boiling solvent always produces an elevation less than the theoretical value. Sometimes a very small addition will lower the apparent boiling-point. This effect always shows up clearly in the graph of change of resistance against concentration (see Fig. 4).

A small amount of inert solute can be added to establish a zero for a determination, and then a weighed amount of the sample. However, greater precision results when a series of additions of solute is made and the elevation (in ohms) is plotted against the weight

* A compact bridge, and also the glass parts of the apparatus are now being manufactured by Messrs. A. Gallenkamp, Sun Street, E.C.1.

added. The slope of this graph gives a more reliable value for a molecular weight than that obtained by a single addition of a similar total weight.

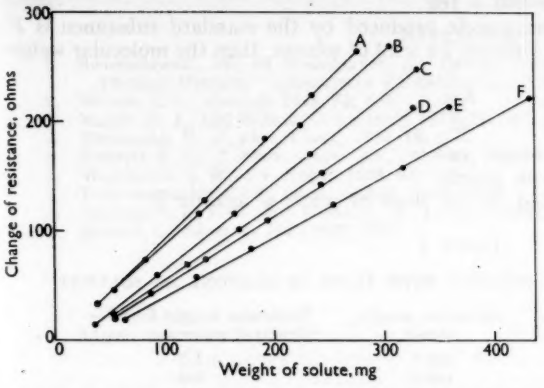

Fig. 4. Relationship between weight of solute and change of resistance: curve A, benzoic acid; curve B, naphthalene; curve C, coumarin; curve D, *m*-dinitrobenzene; curve E, benzidine; curve F, phenyl salicylate

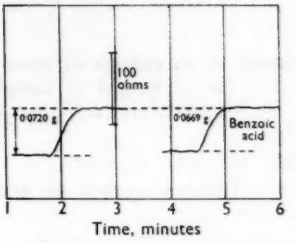

Fig. 5. Change of resistance with time produced by the addition of benzoic acid to 25 ml of boiling acetone. Equilibrium is reached in 1 minute; the 100-ohm step corresponds to a change in temperature of about 0·1°C

PROCEDURE FOR DETERMINING MOLECULAR WEIGHTS—

A typical determination is carried out as follows. Introduce an appropriate volume of solvent by means of a pipette. Light the microburner and adjust its position so that the flame is immediately below the platinum wire sealed into the boiling chamber. Set the flame height at about ½ inch and allow about 5 minutes for the temperature to become steady. Remove the cold-finger condenser and add a few milligrams of sample by way of the side tube. When a definite elevation has been observed, the apparatus is ready for a determination. Bring the galvanometer to zero and note the reading on the decade box. Add a weighed amount of the sample (about 50 mg if 20 ml of solvent are used). Note the reading on the decade box 1 minute after the galvanometer has become steady. The total time for each reading is about 3 minutes and depends on the rate at which the sample dissolves (see Fig. 5).

For solids it is convenient to prepare pellets by means of a press, and to have them ready weighed. Much delay in making the observations can lead to serious errors if the barometric pressure is not steady.[1] Liquids are added with a teat-pipette, 3 or 4 drops at a time. The pipette is weighed in a specimen tube together with the sample, and the amount added is found by difference.

A total weight of about 200 mg added in four portions will give a result reliable to within ±2 per cent. for most solutes, and for pure solids an error of ±0·8 per cent. has been obtained. It is important that the elevations for a number of small increments should be measured, especially for liquids. Occasionally, small amounts of sample, particularly of liquids, may not drain completely with the solvent from the condenser tube. This residue is removed when the next addition is made and accounts for most of the scatter in the individual readings.

When the amount of sample is too small to permit this procedure, 30 to 50 mg should be added to, say, 5 ml of solvent followed by an equivalent amount of reference compound.[1] The results obtained by this method are reliable to ±3 per cent.

CALCULATION OF MOLECULAR WEIGHTS—

(*i*) Determine the ratio change in ohms per g-mole of solute in a particular volume of solvent for a standard substance, *e.g.*, for benzoic acid the slope of the graph of weight added against change in resistance with 20 ml of acetone in the ebulliometer was—

$$\frac{360 \text{ ohms}}{0{\cdot}4 \text{ g}} = 900 \text{ ohms per g}$$
$$= 900 \times 122 \text{ ohms per g-mole}$$
$$= 109{,}800 \text{ ohms per g-mole.}$$

(*ii*) Find the ratio change in resistance against weight added for the substance under investigation, *e.g.*, a hydrocarbon was found to give a slope of 260/0·4 = 650 ohms per g. Then the molecular weight is 109,800/650 = 169.

(*iii*) In general, if the change per g-mole produced by the standard substance is K, which may be called the ebulliometer constant for x ml of solvent, then the molecular weight is given by—

$$\frac{Kw}{R},$$

where R = change in resistance in ohms, and
w = weight of sample added in grams.
Alternatively, w/R can be replaced by the slope of graph w against R.

TABLE I

DETERMINATION OF MOLECULAR WEIGHTS WITH 15 ml OF ACETONE AS SOLVENT

Substance	Molecular weight found	Molecular weight found—calculated molecular weight
Naphthalene	129·7	+1·7
m-Dinitrobenzene	168·0	0·0
Benzoic acid	120·8	−1·2
Coumarin	145·8	−0·2
Benzidine	183·0	−1·0
Phenyl salicylate	215·9	+1·9

TABLE II

DETERMINATION OF MOLECULAR WEIGHTS WITH 20 ml OF ACETONE AS SOLVENT

Substance	Molecular weight found	Molecular weight found—calculated molecular weight
Benzoic acid	121·6	−0·4
p-Nitrotoluene	138·0	+1·0
1-Chloro-2:4-dinitrobenzene	201·0	−1·5
p-Toluidine	105·6	−1·4

RESULTS

The molecular weights derived from the slopes of curves shown in Fig. 4 are given in Table I. The determinations were carried out in 15 ml of acetone. The standard deviation of the results in Table I from the theoretical molecular weights is ±0·8 per cent.

The results shown in Table II were obtained by using another thermistor and 20 ml of acetone in a slightly larger apparatus. These results were calculated from a separate calibration with benzoic acid.

The average weight of the individual additions for the results shown in Tables I and II was 63 mg. The standard deviation of the results calculated from each separate addition (in the linear region only) was ±2·1 per cent. This corresponds to an uncertainty of about 1 ohm in each reading, but this error is not cumulative. Normally, sufficient solute should be added to produce an elevation of between 30 and 60 ohms at each addition.

The results obtained with liquids were less precise, *e.g.*, the values for a sample of methyl ricinoleate were 307 ± 4 from the slope produced by four additions, and 306 ± 9 from six direct comparisons with benzoic acid in 5, 10 and 15 ml of acetone.

Benzene requires the addition of a stabilising solute before steady readings can be made; coumarin, methyl ricinoleate and light lubricating oil have been used for this purpose. The following figures were obtained in 25 ml of benzene stabilised with lubricating oil—

Substance	Naphthalene	*m*-Dinitrobenzene	Dibenzylamine
Weight of solute, g	0·3538	0·2594	0·6675
Change in resistance, ohms ..	96·0	53·7	112·2

With naphthalene as the standard, this gives molecular weights of 168 for *m*-dinitrobenzene and 204 for dibenzylamine (theoretical value 197). These figures indicate the possibility that successive determinations can be made in the same solution. The thermistor resistance at the boiling-point of benzene was 8498 ohms and the changes could therefore be measured to 0·1 ohm.

I thank Dr. J. Leicester for his helpful criticism and advice in the preparation of this paper.

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Recommended Methods for the Analysis of Trade Effluents

PREPARED BY THE JOINT A.B.C.M. - S.A.C. COMMITTEE ON METHODS FOR THE ANALYSIS OF TRADE EFFLUENTS

Methods for the Determination of Residual Chlorine, Cyanides and Thiocyanate, Fluoride, Formaldehyde and Sulphite and Thiosulphate

Residual Chlorine

THE residual chlorine content of an effluent sample will tend to decrease after collection, particularly in hot weather and if the chlorine is not in combination with nitrogenous compounds. It is therefore important that residual-chlorine tests be carried out with a minimum of delay; ideally, the examination for chlorine should be made at the actual location of sampling. Provided that results of the highest accuracy are not required, commercial chlorine-testing outfits are useful for such tests made on the spot.

When the sample contains suspended matter, a portion should be allowed to stand for 15 minutes, and the supernatant liquid tested for chlorine.

In all, four methods are given, covering different ranges of chlorine content and the presence or otherwise of certain interfering compounds.

o-TOLIDINE METHOD

PRINCIPLE OF METHOD—

The colour developed by reaction of the residual chlorine with *o*-tolidine is compared with standards.

RANGE—

For residual chlorine contents up to 1·0 mg per litre of sample.

APPLICABILITY—

This method measures total residual chlorine (free and combined). Nitrites and ferric and manganic compounds may interfere: results are acceptable without correction if the sample contains less than 0·2 mg per litre of ferric iron or nitrite nitrogen, or less than 0·01 mg per litre of manganese in the oxidised form. When interfering oxidants are present in amounts exceeding those stated, they are separately determined after removal of the free chlorine by arsenite and the value obtained is subtracted from the uncorrected result. The interference by nitrites is more marked if the sample is unduly exposed to daylight during the test.

REAGENTS—

Hydrochloric acid, diluted (1 + 9).

o-Tolidine solution—Dissolve 1·35 g of *o*-tolidine hydrochloride in 1 litre of diluted hydrochloric acid (1 + 9). The solution must be stored in an amber bottle. Reagent of satisfactory quality can be purchased; if necessary, it can be prepared from less pure material by recrystallising from hot dilute hydrochloric acid solution after decolorising with activated carbon.

Sodium arsenite solution—Dissolve 0·5 g of sodium meta-arsenite, $NaAsO_2$, in distilled water and dilute to 100 ml.

Chlorine standards—Owing to the complications involved in setting up standards actually based on chlorine and to their relative instability, it has long been customary to compare the *o*-tolidine colours either with standard solutions containing dichromate or with coloured-glass standards. Since many laboratories are now equipped with absorptiometers, directions are also given for the preparation of the necessary "temporary" standards, which can conveniently be prepared from hypochlorite.

(*a*) *Permanent solution standards*—

Acid copper sulphate solution—Dissolve 1·5 g of copper sulphate, $CuSO_4.5H_2O$, in distilled water, add 1 ml of sulphuric acid, sp.gr. 1·84, and dilute to 100 ml.

Acid potassium dichromate solution—Dissolve 0·25 g of potassium dichromate in distilled water, add 1 ml of sulphuric acid, sp.gr. 1·84, and dilute to 1 litre.

Permanent standards to match the colours produced by various concentrations of chlorine are prepared according to Table I. Mix the appropriate volumes of the acid copper sulphate and acid potassium dichromate solutions and dilute to 100 ml with distilled water.

TABLE I

PERMANENT SOLUTION STANDARDS FOR USE IN *o*-TOLIDINE TEST FOR RESIDUAL CHLORINE

Chlorine, mg per litre	Acid copper sulphate solution, ml	Acid potassium dichromate solution, ml	Chlorine, mg per litre	Acid copper sulphate solution, ml	Acid potassium dichromate solution, ml
0·01	0·0	0·8	0·25	1·9	25·0
0·02	0·0	2·1	0·30	1·9	30·0
0·03	0·0	3·2	0·35	1·9	34·0
0·04	0·0	4·3	0·40	2·0	38·0
0·05	0·4	5·5	0·50	2·0	45·0
0·06	0·8	6·6	0·60	2·0	51·0
0·07	1·2	7·5	0·70	2·0	58·0
0·08	1·5	8·2	0·80	2·0	63·0
0·09	1·7	9·0	0·90	2·0	67·0
0·10	1·8	10·0	1·00	2·0	72·0
0·20	1·9	20·0			

(*b*) *Coloured-glass standards*—

These are supplied with testing outfits and it is essential to follow exactly the instructions of the manufacturers for the preparation and use of the reagents.

(*c*) *Temporary chlorine standards*—

Prepare a stock solution of sodium hypochlorite to contain approximately 1 per cent. of available chlorine. Determine the concentration of this solution immediately before use by delivering a known volume into an excess of 0·1 *N* sodium arsenite (containing sodium bicarbonate) and titrating the excess with 0·1 *N* iodine solution, using starch as indicator.

In the preparation of temporary chlorine standards the distilled water must be completely free from ammonia and of zero chlorine demand. To this end, ammonia-free water (prepared by distilling tap-water to which sulphuric acid and a few crystals of potassium permanganate have been added) is dosed with sufficient dilute sodium hypochlorite to give a residual chlorine reaction of about 1 mg per litre after 30 minutes. The chlorinated water (in a glass-stoppered bottle) is then allowed to stand in direct sunlight until no residual chlorine is detected when 50 ml are tested with *o*-tolidine solution. The dissipation of the excess of chlorine may take some days, even in strong sunlight.

All glassware to be used in the calibration and test should be filled with heavily chlorinated water for some hours, afterwards being rinsed thoroughly with zero-demand water.

PROCEDURE—

Should the effluent have a total alkalinity (measured as described under "Preliminary Examination of the Sample: Alkalinity") exceeding 400 mg per litre (as $CaCO_3$), add sufficient dilute hydrochloric acid to reduce the alkalinity to this figure. Carry out the test on this adjusted sample, and allow for the dilution when calculating the result.

To 100 ml of the effluent sample (adjusted if necessary) add 1 ml of *o*-tolidine solution and mix rapidly. If the temperature of the sample is less than 20° C,

raise it quickly to that temperature after the *o*-tolidine has been added. Allow the solution to stand in the dark for 15 minutes; then determine the chlorine content by one of the following procedures.

Use of permanent solution standards—Compare the test solutions with the standard solutions in Nessler cylinders: the colours must be viewed from above in north daylight, and not in sunlight. It must be emphasised that the amounts of copper and dichromate solutions required to match the colour produced by a given chlorine content are somewhat dependent on the depth of liquid viewed.

Permanent solution standards should only be used when the test samples are free from appreciable colour or turbidity. When they are used, results should be reported as follows—

For chlorine contents less than 0·1 mg per litre—to nearest 0·01 mg per litre.
For chlorine contents between 0·1 and 0·4 mg per litre—to nearest 0·05 mg per litre.
For chlorine contents more than 0·4 mg per litre—to nearest 0·1 mg per litre.

Use of coloured-glass standards—Proprietary testing outfits should only be used in accordance with the makers' instructions, and the analyst must make sure that the results so obtained agree with those given by either of the two other procedures. Testing outfits are useful for field work, and are especially valuable because they readily permit compensation for colour and turbidity by placing behind the standard glass a control tube containing a portion of the sample that has not been treated with the *o*-tolidine solution. It is recommended, however, that this control tube should contain a portion of the sample that has been acidified (1 ml of diluted hydrochloric acid (1 + 9) per 100 ml) in case acid-soluble suspended matter is present.

Instrumental method—Measure the optical density of the test solution in a spectrophotometer or in an absorptiometer, using a 1-cm cell and a wavelength of 4350 A in a spectrophotometer or a suitable violet filter in an absorptiometer. Use distilled water in the comparison cell. Read the number of milligrams of chlorine equivalent to the observed optical density from a previously prepared calibration graph and, after allowing for any initial dilution of the sample, obtain the net measure of residual chlorine in it.

Establish the calibration graph as follows—

From the stock hypochlorite solution, prepare a series of standards covering the range 0·02 to 1·0 mg of available chlorine per litre, using zero-demand water at a temperature of 20° to 22° C for the dilutions. Do not prepare more than two or three of these diluted solutions at a time, and add the *o*-tolidine reagent (as described for the test solution) immediately afterwards. Allow the solutions to stand for 15 minutes in the dark and then measure the optical densities in 1-cm cells, using distilled water in the comparison cell. Construct a graph relating the optical densities to the number of milligrams of chlorine per litre.

Whichever method of determination is used (instrumental or visual colour comparison), express the result as milligrams of residual chlorine per litre of sample.

To correct for colour or turbidity, measure also the optical density of the sample after addition of 1 ml of diluted hydrochloric acid (1 + 9), using the same cell-length and wavelength or filter as before. Subtract the value obtained from the gross optical density previously measured in the presence of *o*-tolidine; the difference then corresponds to the true residual chlorine content.

Samples containing oxidising agents—To 100 ml of the sample add 2 ml of sodium arsenite solution, mix and at once add 1 ml of *o*-tolidine solution. Mix again and raise the temperature to 20° C if necessary. Allow the solution to stand in the dark for 15 minutes: any colour that develops will be due to interfering oxidants. Measure it in terms of residual chlorine content and subtract the value obtained from the gross value for residual chlorine to give the true chlorine content.

IODIMETRIC METHOD

PRINCIPLE OF METHOD—

Iodine is liberated from potassium iodide by the chlorine and is titrated with sodium thiosulphate solution.

RANGE—

The method is suitable for residual chlorine contents in the range 1 to 10 mg per litre of sample. Higher concentrations can be determined by suitably adjusting the volume of the sample and, if necessary, the concentrations and amounts of the reagents.

APPLICABILITY—

Nitrites and ferric and manganic compounds interfere with the method, which involves titration in dilute acetic acid. When these substances are present, the titre obtained within the pH range 4·5 to 8·0 will usually approximate to the true chlorine equivalent.

It must be stated whether or not the titration was made in acid solution.

REAGENTS—

Potassium iodide solution, 10 *per cent. w/v.*

Acetic acid, glacial.

Potassium iodate solution, 0·005 N—This solution may conveniently be prepared by diluting a stronger standard solution (*e.g.*, the *N*/80 solution used in the Permanganate Value test (see "Oxygen Demand"), 100 ml diluted to 250 ml).

Sodium thiosulphate solution A (*approximately* 0·25 N)—Dissolve 63 g of sodium thiosulphate, $Na_2S_2O_3.5H_2O$, in 1 litre of boiled and cooled distilled water.

Sodium thiosulphate solution B (*approximately* 0·005 N)—Dilute 20·0 ml of solution A to 1 litre. This solution must be standardised immediately before use with standard potassium iodate solution, as follows—

> Cool 500 ml of distilled water to below 20° C, add 10·0 ml of 0·005 *N* potassium iodate solution, and then 5 ml of potassium iodide solution and 5 ml of acetic acid. Mix and allow the solution to stand for 1 minute. Titrate with sodium thiosulphate solution B, with constant swirling, until the colour of the liberated iodine is nearly discharged; then add 2 ml of starch indicator solution and continue the titration until the blue colour disappears for at least 30 seconds.

Starch indicator solution.

PROCEDURE—

Not more than 2 mg of ferric iron per litre should be present; nitrites and oxidised manganese must be absent.

Should the effluent have a total alkalinity (measured as described under "Preliminary Examination of the Sample: Alkalinity") exceeding 400 mg per litre (as $CaCO_3$), add sufficient dilute hydrochloric acid to reduce the alkalinity to this figure. Carry out the test on this adjusted sample and allow for the dilution when calculating the result.

Cool 500 ml of the sample (adjusted if necessary) to below 20° C, add 5 ml of potassium iodide solution (or 0·5 g of solid potassium iodide) and 5 ml of acetic acid. Mix and at once titrate with sodium thiosulphate solution B until the colour of the liberated iodine is nearly discharged; then add 2 ml of starch indicator solution and continue the titration until the blue colour disappears for at least 30 seconds.

1 ml of 0·005 *N* thiosulphate ≡ 0·1773 mg of chlorine.

Express the result as milligrams of residual chlorine per litre of sample.

Modification when nitrite, oxidised manganese or more than 2 mg of ferric iron per litre are present—Adjust the pH of the sample to between 4·5 and 8·0 by addition of acetic acid (or sodium acetate) as necessary. Titrate the solution as described above, but omit the addition of any further acetic acid.

NOTE—If there were transient existence of dichloramine in an effluent, the neutral titration might give low results: such a circumstance would, however, seldom occur.

Cyanides and Thiocyanate

THREE methods are given.

In the *Titration Method*,[1] which is applicable to the higher concentrations of cyanide, a preliminary distillation with acid cuprous chloride is used for the determination of *total* cyanide: any complex cyanides that produce hydrogen cyanide under these conditions will be included. However, by the use of lead acetate instead of acid cuprous chloride, ferrocyanide (which is relatively non-toxic) is excluded and can be separately determined in the residue after distillation.

Aldridge's Method,[2] which is applicable to low concentrations of cyanide, is used for the determination of any compounds that produce thiocyanate or cyanide radicles under the conditions of the test: ferrocyanide, ferricyanide and cyanate are not determined. A modification is given for the separate determination of thiocyanate.

In the *Ferric Thiocyanate Method*, thiocyanate *alone* is determined.

Any determination of cyanide should be made as soon as possible after the sample has been collected, since many cyanides are relatively unstable. If delay in the analysis is unavoidable, the pH of the sample should be raised to 11 or above by the addition of sodium hydroxide, and the sample subsequently stored in a cool place.

TITRATION METHOD

PRINCIPLE OF METHOD—

After distillation of hydrogen cyanide, the cyanide is titrated directly with silver nitrate, using *p*-dimethylaminobenzylidinerhodanine as indicator.

RANGE—

For cyanide contents (as CN') above 10 mg per litre of sample.

APPARATUS—

An all-glass distillation apparatus, fitted with a splash-head and a vertical water-cooled condenser.

REAGENTS—

Sodium hydroxide solution, approximately 2·5 N.
Silver nitrate solution, 0·1 N *or* 0·01 N.

For use in methods (*a*) and (*c*)—

Acid cuprous chloride solution—A 2 per cent. w/v solution in approximately 5 *N* hydrochloric acid. This solution must be freshly prepared.

Rhodanine indicator solution—A 0·02 per cent. w/v solution of *p*-dimethylaminobenzylidinerhodanine in acetone.

For use in method (*b*)—

Lead acetate solution—Dissolve 200 g of lead acetate, $(CH_3COO)_2Pb.3H_2O$, in 1 litre of distilled water.

Methyl orange indicator solution—A 0·04 per cent. w/v aqueous solution.

PROCEDURE—

(*a*) *Determination of total cyanide, including ferrocyanide*

Measure into the distillation flask a suitable volume of the effluent sample (containing 10 to 15 mg of cyanide ion when the content is less than 200 mg per litre, or containing at least 100 mg of cyanide ion when the content is greater than 200 mg per litre), and adjust the volume to about 400 ml with distilled water. Add 10 ml of acid cuprous chloride solution and assemble the apparatus.

Place a conical flask containing 10 ml of sodium hydroxide solution under the condenser, so that the end dips below the surface. Distil the mixture and, when 50 ml of distillate have been collected in the flask, replace it by a second flask containing 10 ml of sodium hydroxide solution and collect a further 50 ml. If necessary,

continue the distillation into a succession of flasks until all the hydrogen cyanide has been distilled.

Titrate the contents of the flasks separately with 0·01 *N* silver nitrate solution (or 0·1 *N* silver nitrate solution if the cyanide content of the sample is greater than 200 mg per litre), using 2 drops of rhodanine indicator solution in each flask (see Note). The end-point is indicated by the appearance of a red colour. Calculate the cyanide content from the sum of the titrations.

1 ml of 0·01 *N* silver nitrate solution ≡ 0·52 mg of cyanide ion.

NOTE—It is important to use the minimum amount of indicator: an excess masks the end-point of the titration.

(*b*) *Determination of cyanide, excluding ferrocyanide*

Measure into the distillation flask a suitable volume of the effluent sample (containing not more than 200 mg of cyanide in any form) and add mineral acid or sodium hydroxide as necessary to make the solution approximately neutral to methyl orange. Dilute the solution to 400 ml and add 10 ml of lead acetate solution. Proceed to determine the cyanide as in method (*a*), commencing at "Place a conical flask . . ." in the second paragraph.

NOTE—Nickel and copper complex cyanides distil only slowly under the conditions of the test, and distillation may have to be prolonged.

(*c*) *Determination of ferrocyanide*

The residue in the distillation flask after the determination of cyanide in method (*b*) can be used for the determination of ferrocyanide. Dilute the mixture to 400 ml with distilled water and add 10 ml of acid cuprous chloride solution. Proceed to determine the cyanide as in method (*a*), commencing at "Place a conical flask . . ." in the second paragraph.

ALDRIDGE'S METHOD

PRINCIPLE OF METHOD—

In this method, cyanide and thiocyanate are converted to cyanogen bromide, which is then determined colorimetrically as the red compound formed by coupling with benzidine in pyridine solution.

RANGE—

For cyanide contents (as CN′) up to 2 mg per litre of sample (or up to 20 mg per litre, after dilution).

APPLICABILITY—

The method is generally applicable for the determination of any compound that produces –CN or –CNS radicles on acidification. Ferrocyanide, ferricyanide and cyanate are *not* determined.

REAGENTS—

Bromine water, saturated.

Arsenious acid solution—Dissolve 2 g of arsenious oxide, As_2O_3, in 100 ml of distilled water.

Benzidine reagent—Dissolve 5 g of benzidine hydrochloride in 100 ml of distilled water containing 2 ml of hydrochloric acid, sp.gr. 1·18. This solution should be freshly prepared.

Pyridine solution—An approximately 60 per cent. v/v solution in distilled water (the mixture of constant boiling-point).

Acetic acid, approximately 2 N.

Standard cyanide solution—Dissolve 1·25 g of potassium cyanide in 500 ml of distilled water. Standardise this solution frequently with 0·01 *N* silver nitrate solution (1 ml ≡ 0·52 mg of CN′), using rhodanine indicator solution (see "Titration Method"). Adjust the solution so that 1 ml contains 1 mg of CN′.

From this stock solution prepare a dilute solution freshly as required by diluting 10·0 ml to 1 litre with distilled water, and diluting this a further 10 times.

1 ml ≡ 1 μg of cyanide (CN').

PROCEDURE—

(*a*) *Determination of cyanide and thiocyanate*

Into a glass-stoppered tube (calibrated at 10 ml) measure 2 ml of the effluent sample, adjusted by dilution if necessary to contain not more than 2 μg of cyanide ion. Acidify with acetic acid; then add 0·2 ml of bromine water and mix thoroughly. Add 0·2 ml of arsenious acid solution to remove excess of bromine; remove any bromine vapour by blowing across the mouth of the tube. Mix 3 ml of pyridine solution with 0·6 ml of benzidine reagent, add this mixture to the contents of the tube, dilute to the mark with distilled water and mix thoroughly. Stopper the tube and allow the mixture to stand in the dark for 25 to 30 minutes at a temperature between 15° and 20° C.

Carry out a blank determination on all the reagents used.

Proceed to determine the cyanide content (including thiocyanate) colorimetrically, either instrumentally or by visual colour comparison.

Instrumental method—Measure the optical densities of the test and blank solutions in a spectrophotometer or in an absorptiometer, using 1-cm cells, and using a wavelength of 5200 A in a spectrophotometer or a suitable green filter in an absorptiometer. Use distilled water in the comparison cell. Read the number of micrograms of cyanide ion equivalent to the observed optical densities of the test and blank solutions from a previously prepared calibration graph, and so obtain the net measure of cyanide ion in the sample.

Establish the calibration graph as follows—

> Into a series of stoppered tubes measure appropriate amounts of standard cyanide solution, covering the range 0 to 2 μg of cyanide ion, and proceed as for the test solution. Measure the optical densities and construct a graph relating the optical densities to the number of micrograms of cyanide ion.

Visual colour-comparison method—Compare the colour of the test and standard solutions directly in the tubes.

Alternatively, proprietary coloured discs may be used in a comparator instead of the standard solutions, and the makers' instructions should be followed. The analyst must make sure that the results so obtained agree with those given by the recommended method.

Whichever method of determination is used (instrumental or visual colour comparison), express the result in terms of cyanide (as CN') as milligrams per litre of sample.

(*b*) *Separate determinations of cyanide and thiocyanate*

In another tube, acidify a second similar volume of effluent sample with acetic acid. Bubble a stream of air through the solution for about 15 minutes to remove hydrogen cyanide. Add 0·2 ml of bromine water and mix thoroughly; then proceed to determine the cyanide as in method (*a*), commencing at "Add 0·2 ml of arsenious acid. . . ."

This gives the amount of cyanide equivalent to the amount of thiocyanate originally present.

The difference between the two results gives the cyanide originally present as such in the sample.

FERRIC THIOCYANATE METHOD

PRINCIPLE OF METHOD—

The red colour of ferric thiocyanate, produced by the direct addition of a ferric salt, is compared visually with standards.

RANGE—

For thiocyanate contents above 1 mg per litre of sample.

APPLICABILITY—

The method is generally applicable, but mercuric salts and oxalic acid interfere. It is useful as a rapid method of determination, but it is not a method of the highest accuracy since the colour fades in sunlight and its intensity depends on the amount of ferric salt added and on the presence of sulphate.

To compensate for any colour in the sample itself, use is made of mercuric chloride.[3]

REAGENTS—

Hydrochloric acid, approximately 0·1 N.

Ferric chloride solution—Dissolve 10 g of ferric chloride, $FeCl_3.6H_2O$, in 1 litre of distilled water.

Mercuric chloride solution, saturated.

Standard thiocyanate solution—Dissolve about 5 g of potassium thiocyanate in distilled water and dilute to 500 ml. Determine the thiocyanate content by titration with 0·1 *N* silver nitrate solution, using Volhard's method (1 ml of 0·1 *N* $AgNO_3$ ≡ 5·81 mg of CNS'). Adjust the solution so that 1 ml contains 5·0 mg of CNS'.

Dilute 10·0 ml of this solution to 500 ml with distilled water. This dilute solution should be freshly prepared.

1 ml ≡ 0·1 mg of CNS'.

PROCEDURE—

To 50 ml of the filtered effluent sample (or an aliquot diluted to 50 ml) in a Nessler cylinder add 0·5 ml of 0·1 *N* hydrochloric acid and 0·5 ml of ferric chloride solution. To a second cylinder containing rather less than 50 ml of distilled water also add 0·5 ml of hydrochloric acid and 0·5 ml of ferric chloride solution. From a burette add, drop by drop, standard thiocyanate solution to the second cylinder, stirring after each addition, until the colour matches that in the first cylinder. Note the volume of standard thiocyanate used (x ml).

To the first cylinder containing the sample add 1 ml of mercuric chloride solution to discharge the red thiocyanate colour. Compare any residual colour with standard thiocyanate as described above, and note the volume used (y ml).

$$\text{Thiocyanate in sample (mg of CNS' per litre)} = \frac{100\,(x-y)}{\text{Vol. of sample, ml}}$$

NOTE—Great care must be taken to avoid accidental contamination of the contents of the cylinders with mercuric chloride.

REFERENCES

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3. Ministry of Housing and Local Government, "Methods of Chemical Analysis as applied to Sewage and Sewage Effluents," Second Edition, H.M. Stationery Office, 1956, p. 74.

Fluoride

PRINCIPLE OF METHOD—

In this method,[1] after removal of free chlorine by arsenite, fluorine is steam-distilled as hydrofluorosilicic acid in the presence of perchloric acid; the fluoride ion is determined by titration, which depends on the bleaching action of fluoride on the thorium lake of alizarin red S.

RANGE—

For fluoride contents (as F') between 0·5 and 5 mg per litre of sample.

APPLICABILITY—

The method is generally applicable.

APPARATUS—

Distillation apparatus—The apparatus, of borosilicate glass, consists of a 100-ml Claissen flask connected to a water-cooled condenser by means of the side-tube. The neck carries a thermometer and a steam-inlet tube, both reaching nearly to the bottom of the flask.

The water used for steam generation *must* be made alkaline with sodium hydroxide.

REAGENTS—

Sodium arsenite solution, 1 per cent. w/v.

Perchloric acid, 60 per cent.

Hydrochloric acid, 0·05 N.

Sodium hydroxide solution, 0·05 N.

Thorium nitrate solution—Dissolve 0·25 g of thorium nitrate, $Th(NO_3)_4.4H_2O$, in distilled water and dilute to 1 litre.

Alizarin red S solution, 0·01 per cent.

Standard fluoride solution—Dissolve 0·221 g of dry sodium fluoride in distilled water and dilute to 100 ml. Dilute 10·0 ml of this solution to 1 litre.

1 ml ≡ 0·01 mg of fluoride (as F').

Silver sulphate.

Calcium oxide (fluoride-free)—This can be prepared by the following method—

Prepare an ammonium carbonate reagent by dissolving 110 g of ammonium carbonate (analytical-reagent grade) and 55 ml of ammonium hydroxide, sp.gr. 0·880, in distilled water and diluting to 600 ml.

Dissolve 200 g of analytical-reagent grade dried calcium chloride (70 to 75 per cent. $CaCl_2$) in about 600 ml of warm distilled water. Stir into this solution 20 ml of ammonium carbonate reagent, bring the mixture just to the boiling-point, allow the precipitate to settle for a few minutes and collect it on a Buchner funnel, using suction. Reject the precipitate. Repeat the precipitation and filtration three times, using 20 ml of ammonium carbonate reagent each time. Finally, treat the clear filtrate from the last precipitation with the remainder of the ammonium carbonate reagent, stir the mixture well and bring it just to the boiling-point. Allow the precipitate to settle, collect it on a filter and wash it several times with hot distilled water until free from chloride. Dry it at 100° C and ignite to oxide in a platinum dish in amounts of 1 to 2 g as required.

Methyl orange indicator solution—A 0·04 per cent. w/v aqueous solution.

(*a*) PROCEDURE FOR EFFLUENTS KNOWN TO BE FREE FROM APPRECIABLE AMOUNTS OF ORGANIC MATTER—

Remove any free chlorine by adding sufficient (but not an excess of) sodium arsenite solution.

Preparation of apparatus—Into the Claissen flask measure 0·2 g of silver sulphate (see Note), 7 ml of distilled water and 15 ml of perchloric acid, and add a number of fragments of borosilicate glass (or glass-wool if "bumping" is experienced). Heat the flask until the temperature reaches 120° to 125° C, connect the steam supply and distil the contents at a temperature of 137° to 140° C. Distil 150 ml during 25 to 35 minutes, steam out the condenser and discard the distillate.

Determination of blank—Proceed to steam-distil a further 150 ml, and determine the fluoride in the distillate by the method described below. The figure for the blank should not exceed 0·0015 mg of fluoride and should remain approximately constant for further 150-ml fractions.

Determination of fluoride—Cool the contents of the flask and add 20 ml of the effluent sample, rinsing the neck of the flask with 1 to 2 ml of distilled water. Connect the steam supply and distil 150 ml as described above.

Determine the acidity of the distillate as follows—

In a 100-ml Nessler cylinder, titrate 50 ml of the well mixed distillate with 0·05 *N* sodium hydroxide solution, using a drop of methyl orange indicator

solution, until the colour matches that in a similar cylinder containing an equal volume of distilled water and a drop of methyl orange indicator solution.

Transfer the remaining 100 ml of distillate (or a suitable aliquot diluted to 100 ml, if the fluoride content is high) to a Nessler cylinder and add the requisite amount of 0·05 *N* hydrochloric acid to make the total acidity equal to 5·0 ml of 0·05 *N* acid. Prepare a control cylinder containing 5·0 ml of 0·05 *N* hydrochloric acid diluted to the same volume with distilled water, and add to both cylinders 3 ml of alizarin red S solution. To the test cylinder add thorium nitrate solution from a burette until a slight pink colour persists when compared with the yellow of the control cylinder. Add an exactly similar volume of thorium nitrate solution to the control cylinder, which then becomes more pink than the test cylinder; then add slowly from a burette (graduated at 0·02-ml intervals) standard fluoride solution until the tints of the test and control solutions match. The volume of standard fluoride solution added corresponds to the amount of fluoride present in the portion of test distillate taken.

Calculate the amount of fluoride present in 150 ml of distillate, subtract the figure obtained for the blank and express the net fluoride content as milligrams per litre of sample.

(*b*) PROCEDURE FOR EFFLUENTS CONTAINING APPRECIABLE AMOUNTS OF ORGANIC MATTER—

Measure 20 ml of the effluent sample into a platinum basin, add 1 g of fluoride-free calcium oxide and evaporate the contents to dryness on a water bath. Transfer the basin and residue to a muffle furnace maintained at approximately 600° C, ignite for 1½ to 2 hours, and cool. Using not more than 20 ml of distilled water acidified with perchloric acid, wash the contents of the basin into the distillation flask and proceed to determine the fluoride content as described under (*a*) above.

NOTE—The silver sulphate added must be in excess of the equivalent amount of chloride present in the effluent and more than 0·2 g should be added if necessary.

REFERENCE

1. Analytical Methods Committee, *Analyst*, 1944, **69**, 243.

Formaldehyde

PRINCIPLE OF METHOD—

In this method,[1] the formaldehyde reacts with acetylacetone in the presence of an excess of an ammonium salt to form a yellow compound, diacetyldihydrolutidine, which is determined colorimetrically.

RANGE—

For formaldehyde contents up to 8 mg per litre of sample.

APPLICABILITY—

Distillation of the sample is included to reduce interference. A full investigation of interfering substances has not been made, but it is known that phenols up to 200 mg per litre do not interfere.

REAGENTS—

Acetylacetone reagent—Dissolve 150 g of ammonium acetate in distilled water, add 3 ml of glacial acetic acid and 2 ml of acetylacetone, and dilute to 1 litre with distilled water.

Sodium sulphite solution—Dissolve 250 g of sodium sulphite, $Na_2SO_3.7H_2O$, in 1 litre of distilled water.

Sulphuric acid, N.

Standard formaldehyde solution—Determine the formaldehyde content of technical formaldehyde solution (about 40 per cent. w/v of formaldehyde) as follows—

Weigh about 6 g of technical formaldehyde solution into a 100-ml calibrated flask and dilute to the mark with distilled water. Measure 25 ml from

a pipette into a 250-ml flask, add a drop of thymolphthalein indicator solution and neutralise with *N* sodium hydroxide solution. Add 2 drops of thymolphthalein indicator solution to 50 ml of sodium sulphite solution and neutralise it. Add this sodium sulphite solution to the neutralised formaldehyde solution, mix and titrate the liberated sodium hydroxide with *N* sulphuric acid.

1 ml of *N* sulphuric acid ≡ 0·03003 g of formaldehyde.

Calculate the formaldehyde content of the diluted formaldehyde solution, and immediately before use prepare a solution such that—

1 ml ≡ 0·1 mg of formaldehyde.

Thymolphthalein indicator solution—A 0·1 per cent. solution in ethanol.

PROCEDURE—

Transfer 50 ml of the effluent sample (containing not more than 8 mg of formaldehyde per litre) to a 100-ml flask. Acidify slightly with dilute sulphuric acid and add 10 ml of distilled water. Connect the flask by means of a glass joint to a water-cooled condenser and distil 50 ml of the solution into a 100-ml measuring cylinder. Add 50 ml of acetylacetone reagent, and transfer the mixture to a stoppered flask and heat it at 60° C for 10 minutes.

Carry out a blank procedure on all the reagents used.

Cool the solutions and measure the optical densities in a spectrophotometer or in an absorptiometer, using a 1-cm cell and using a wavelength of 4250 A in a spectrophotometer or a suitable violet filter in an absorptiometer. Use distilled water in the comparison cell. Read the number of milligrams of formaldehyde equivalent to the observed optical densities of the test and blank solutions from a previously prepared calibration graph, and so obtain the net measure of formaldehyde in the sample.

Establish the calibration graph as follows—

Into a series of stoppered flasks, measure appropriate amounts of the diluted standard formaldehyde solution, covering the range 0 to 8 mg of formaldehyde per litre, and dilute each to 50 ml. Add 50 ml of acetylacetone reagent and proceed as for the sample. Measure the optical densities, using a 1-cm cell, and construct a graph relating the optical densities to the number of milligrams of formaldehyde.

Express the result as milligrams of formaldehyde per litre of sample.

NOTE—If the effluent sample contains more than 8 mg of formaldehyde per litre, dilute appropriately.

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1. Nash, T., *Biochem. J.*, 1953, **55**, 416.

Sulphite and Thiosulphate

PRINCIPLE OF METHOD—

In this method,[1] the total iodine equivalent of sulphite and thiosulphate is determined; in a separate portion sulphite is masked by formaldehyde and the iodine equivalent of the thiosulphate is determined.

RANGE—

For sulphite contents (as SO_3'') greater than 2 mg per litre of sample, and for thiosulphate contents (as S_2O_3'') greater than 5 mg per litre of sample.

APPLICABILITY—

The method is generally applicable. Sulphide interferes and, if present, is first removed as zinc sulphide.

REAGENTS—

Hydrochloric acid, sp.gr. 1·18.

Acetic acid, glacial.

Zinc acetate solution, 25 *per cent. w/v.*
or
Zinc carbonate, finely divided.
Formaldehyde solution, 40 *per cent. w/v.*
Potassium iodide solution, 10 *per cent. w/v.*
Iodine solution, 0·01 N—This solution should be freshly prepared.
Sodium thiosulphate solution, 0·01 N—This solution should be freshly prepared.
Starch indicator solution.

PROCEDURE—

Sulphite and thiosulphate—If sulphide is present in the effluent sample, add sufficient zinc acetate solution to precipitate the sulphide and filter off the zinc sulphide. Alternatively, shake the sample with an excess of finely divided zinc carbonate, allow the precipitate to settle and then filter. If sulphide is to be determined, retain the precipitate.

Measure 200 ml of the filtrate (or of the effluent sample if sulphide is known to be absent) into a 500-ml flask containing 25·0 ml of 0·01 *N* iodine solution and 2 ml of hydrochloric acid, pouring the sample carefully down the side of the flask and mixing gently. Titrate the excess of iodine with 0·01 *N* sodium thiosulphate solution, adding the starch indicator solution near the end-point.

Thiosulphate alone—To a further 200 ml of effluent sample or filtrate add 5 ml of formaldehyde solution, and then 2 ml of acetic acid and 2 ml of potassium iodide solution. Titrate with 0·01 *N* iodine solution, using starch indicator solution.

The difference between the two values for the iodine equivalents gives that of the sulphite.

1 ml of 0·01 *N* iodine solution $\equiv$ 0·4 mg of sulphite (as SO_3''), or
$\equiv$ 0·56 mg of thiosulphate (as S_2O_3'').

Express the results as milligrams of sulphite or thiosulphate per litre of sample.

REFERENCE

1. Fogg, D. N., and Wilkinson, N. T., *J. Appl. Chem.*, 1952, **2**, 357.

Notes

THE DETERMINATION OF OXYGEN IN BERYLLIUM BY THE MICRO VACUUM FUSION METHOD

IN a recent paper,[1] we pointed out that the determination of oxygen in beryllium by the micro vacuum fusion method was unsatisfactory and that further investigation was required.

This has now resulted in the development of a method that appears to be equally as satisfactory as that described for titanium, zirconium and so on.

EXPERIMENTAL

The apparatus, sample preparation, etc., were as previously described.[1] A pre-requisite in this investigation was a sample of beryllium in which the distribution of oxygen was uniform. In the preliminary work, most of the materials examined showed considerable heterogeneity with respect to oxygen content, but eventually a rod that had been fabricated by powder extrusion was obtained, which from analyses by a chemical method[2] appeared to be suitable as a reference sample.

Numerous variants of the technique used in the analysis of zirconium were tried with this sample, but without success, it being apparently impossible to achieve satisfactory solution of the beryllium in the platinum "bath." The problem was eventually solved by the addition of about 60 mg of tin foil to the bath, both before the addition of any beryllium and together with each sample. This had a spectacular effect as regards suppression of the evaporation of the beryllium, and the results for oxygen were consistent and in excellent agreement with those by a chemical method.[2]

OXYGEN DETERMINATION IN BERYLLIUM ROD—

An experiment was carried out with sample weights of 20 to 30 mg and at a temperature of 1950° ± 20° C. The bath contained 3 g of platinum and 60 to 70 mg of tin were added with each sample, the results being as follows—

Oxygen found, % .. .. .. 0·30 0·27 0·31

Oxygen found by chemical method, % 0·31 (mean of 6 determinations) Standard deviation = ± 0·03%

This experiment was repeated with smaller sample weights (7 to 12 mg), so that the amount of beryllium in the bath was reasonably small. Two different series of determinations gave the following results—

(*a*) Oxygen found, % 0·26 0·29 0·36 0·29 0·31 0·30

(*b*) Oxygen found, % 0·30 0·26 0·30 0·30 0·30 0·27 0·23 0·24 0·19 <0·1

In series (*b*), a bluish violet discharge occurred in the furnace tube during the analysis of the last three samples. This discharge had been observed sporadically in earlier experiments, but hitherto had been of short duration and could be extinguished by switching the heater off momentarily. In this instance, however, it was continuous, could not be extinguished and is thought to indicate the presence of beryllium vapour. Repetition of series (*b*) gave 0·36, 0·30, 0·27, 0·32, 0·29, 0·32, 0·28, 0·19 and 0·15 per cent. of oxygen.

The "fall off" in apparent oxygen content continued to appear in subsequent experiments, despite variations made in the amounts and ratios of beryllium, tin and platinum. Occasionally, nine or ten samples (equivalent to 120 to 150 mg of beryllium) have been analysed before the fall off is observed, but it is thought that six to eight samples are all that can be safely dealt with in one series.

Nevertheless, it was considered that a satisfactory technique had been established and analyses were carried out on various other types of material, the agreement between the results from the chemical and vacuum fusion methods being satisfactory.

OXYGEN DETERMINATION IN BERYLLIUM POWDER—

As a final check, the method was applied to a sample of −200-mesh B.S.S. beryllium powder. The sample weights taken were 8 to 14 mg enclosed in platinum tubing and the temperature used was 1950° ± 20° C. The bath contained 3 g of platinum and 60 to 70 mg of tin were added with each sample, the results being as follows—

Oxygen found, % 1·0 0·72 0·73 1·0 0·92 0·93 0·82 0·86 0·63 0·73 0·93 0·73 0·84 0·96 0·82 1·0

Mean = 0·85% Standard deviation = ±0·09%

Oxygen found by chemical method, % 0·83 (mean of 10 determinations) Standard deviation = ± 0·07%

CONCLUSIONS

The micro vacuum fusion method has been successfully applied to the determination of oxygen in beryllium.

With many of the samples examined, the spread of results is such that a single determination may not produce a figure representative of the bulk material. This, however, must be attributed to non-uniform distribution of oxygen in the metal, since results on the reference sample have repeatedly shown a coefficient of variation of 8 per cent., which is generally conceded to be satisfactory.

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THE DETERMINATION OF THE OXYGEN CONTENT OF SODIUM METAL BY THE BUTYL BROMIDE METHOD

THE success of determining the oxygen content of sodium metal by the butyl bromide method[1,2,3] in the parts per million range depends largely on accurate acidimetric end-point detection by using indicators or potentiometric end-point methods. After the reaction between the sodium metal and the butyl bromide, the bromide - oxide mixture is dissolved in water. The dilute sodium

hydroxide solution (0·001 to 0·05 *N*), containing 5 to 8 g of sodium bromide, is titrated with dilute hydrochloric acid, and recognition of the end-point, even when a glass electrode indifferent to the presence of sodium ions is used, is subject to large error (see Fig. 1).

Consideration was given to the use of ethanol as the solvent in the titration instead of water. The low solubility of sodium bromide in ethanol (2·3 g in 100 g at 29° C[4]) would result in a lowering of the effective concentration of sodium bromide. A statistical survey was made of the accuracy of detecting the end-point in aqueous solutions (see Fig. 1) and in water - ethanol mixtures (see Fig. 2).

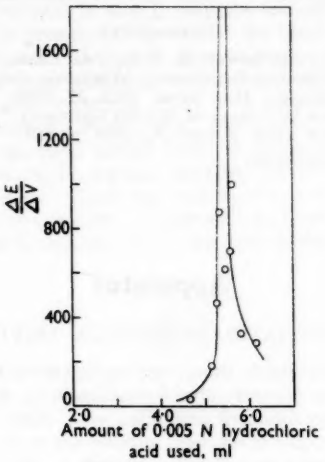

Fig. 1. Potentiometric titration of 10 ml of 0·002 *N* sodium hydroxide (diluted to 100 ml) containing 5 g of sodium bromide against 0·005 *N* hydrochloric acid

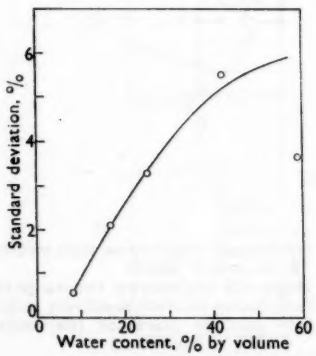

Fig. 2. Influence of the presence of water in a titration mixture containing sodium bromide on the standard deviation

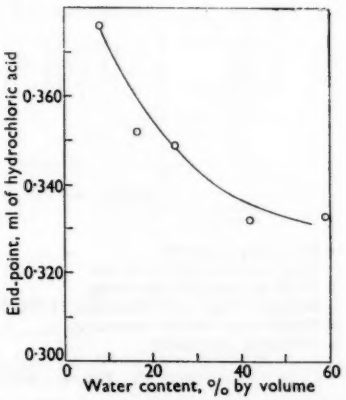

Fig. 3. Depression of the end-point owing to the presence of water

Experimental

Ten millilitres of 0·002 *N* sodium hydroxide diluted to 30 ml with water - ethanol mixture were saturated with bromide and titrated against 0·05 *N* hydrochloric acid from a microburette with methyl red as indicator, no precautions being taken to eliminate the effect of carbon dioxide. A series of eight titrations was carried out with a progressive increase in the water

content of the solution. The standard deviation was plotted against the water content (see Fig. 2). It was also noted that the absolute amount of titrant decreased as the water content of the mixture increased. This was shown by plotting the average end-points against the water content (see Fig. 3).

It is evident that the titration can be carried out with good precision and accuracy with the use of indicators by ensuring that the water content of the sodium hydroxide solution (containing sodium bromide) does not exceed 10 per cent. by volume. It is recommended that the sodium monoxide - sodium bromide mixture should be allowed to react with the requisite volume of a 90 to 95 per cent. by volume ethanol - water mixture when following the specified procedure.

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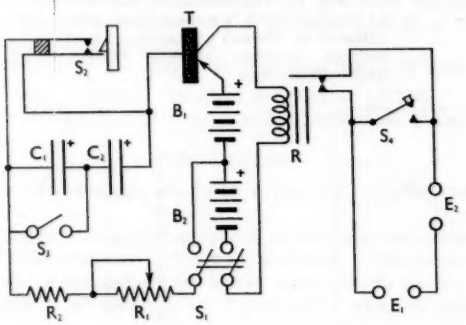
Apparatus

A TRANSISTOR-OPERATED DISPENSING DEVICE FOR LIQUIDS

CONSISTING essentially of a controllable timer, the arrangement shown in Fig. 1 is used in conjunction with an electromagnetic control valve[1,2] for dispensing fixed volumes of liquids, such as indicators or stains, and for the filling of ampoules, etc. Since reagent additions can be progressively cut down as the end-point is reached, another use is for routine or remotely controlled titrimetry. All parts are enclosed in a 6-inch × 6-inch × 4-inch high box.



B_1, B_2 = 6-volt dry batteries
C_1 = 10-μF electrolytic condenser
C_2 = 50-μF electrolytic condenser
R = Sensitive relay, coil resistance 11,500 ohms
R_1 = 50,000-ohm variable resistance
R_2 = 1000-ohm resistance
S_1 = Double-pole single-throw main switch
S_2 = "Brief-contact" switch
S_3 = Single-pole single-throw time-range switch
S_4 = Push-button continuous-delivery switch
T = PHP junction transistor (Raytheon type CK722, or equivalent)

Fig. 1. Circuit diagram of control unit

When main switch S_1 is closed, current from battery B_1 can flow briefly through the base-emitter path of transistor T and through resistances R_1 and R_2, thereby charging condensers C_1 and C_2. When charging is complete, the base-emitter current falls almost to zero and greatly reduces the current in the collector-emitter path. The contacts of relay R then open and flow of liquid ceases. Depression of the "brief-contact" switch, S_2, short circuits the condensers and causes liquid to be delivered until charging is again complete. For a given condenser, the period of charging, and hence of delivery, increases as the effective resistance of R_1 is increased. With switch S_3 closed, R_1 can be set to give any delivery time within the approximate limits of 1 to 8

seconds. When S_3 is opened, both limits are reduced by a factor of about 6. This permits delivery per impulse of a single drop or less. Continuous delivery is obtained by depressing the push-button switch, S_4.

The construction of the "brief-contact" switch is shown in Fig. 2. The frame, A, of 18-gauge sheet metal, has two holes, BB, by which it can be bolted to the underside of the control panel. Screwed to the frame is hardwood mount C, which carries spring contact blades D and E. These and their separators were taken from an old telephone relay, and are set with a contact gap of about 0·01 inch. Hardwood operating block F, normally forced upwards by spring G, is mounted on two axially disposed wood-screws, H and I, only the smooth unthreaded portions of which project from the block. Since it presses lightly against the back of the frame, the block cannot rotate, but can move up and down. It carries sheet-steel pawl J, the tip of which is smooth, slightly radiused and preferably case-hardened. The projection of J from the block is adjusted by cam K, which, as can be seen from Fig. 2 (*d*), is a short length of brass tubing sweated eccentrically on to the upper part of a wood-screw. The projection is adjusted by trial until, on depression of push-button L, the pawl carries blade D downwards for about $\frac{1}{8}$ inch and then releases it. This blade over-shoots its normal position, momentarily closing the contacts and thereby discharging the condensers. When the push-button is released, the pawl swings slightly about its axis and does not close the contacts. If the switch cannot be used in the vertical position, the gravity arm M of the pawl is replaced by a very light spring.

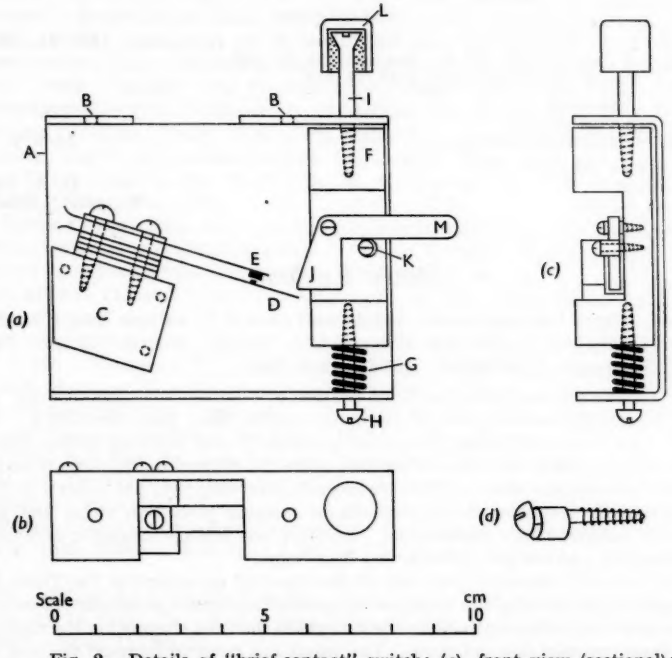


Fig. 2. Details of "brief-contact" switch: (*a*), front view (sectional); (*b*), top view (diagrammatic); (*c*), side view (sectional); (*d*), enlargement of cam, K

Any positive-acting sensitive relay can be used, provided that the contacts close with an input not greater than 1 mA and re-open when the current falls to about 0·5 mA. The voltage of battery B_2 can be reduced if a relay of coil resistance less than 10,000 ohms is available. If this resistance is not more than about 5000 ohms, B_2 can be omitted and, by slight re-wiring, a single-pole switch can then be used for S_1. Since the drain on the batteries is only about 1 mA, replacement is governed mainly by shelf-life. The solenoid of the liquid control valve and the appropriate power supply are connected to terminal pairs E_1 and E_2, respectively.

TABLE I

DELIVERY OF WATER PER DEPRESSION OF THE PUSH-BUTTON

	Volume of water delivered, ml				
With S_2 closed—	0·24	0·23	0·26	0·22	0·22*
	0·37	0·35	0·34	0·33	0·35
	0·65	0·63	0·67	0·63	0·66
	1·10	1·08	1·11	1·13	1·10
	1·95	1·93	1·97	1·91	1·93†
With S_2 open—	0·04	0·04	0·05	0·06	0·04*
	0·14	0·12	0·13	0·16	0·12
	0·32	0·29	0·36	0·31	0·35†

*R_1 set at minimum resistance. † R_1 set at maximum resistance.

For a given setting of R_1, the volume delivered per depression of L naturally depends upon the hydrostatic pressure and the outlet resistance, including that of the control valve. For best results, the valve should have a small lift and a fairly low resistance, the actual rate of flow being fixed by a fine-control stopcock[3] mounted above the valve. Reproducibility is largely dependent on control-valve characteristics; typical results for sets of 5 successive deliveries are given in Table I. These refer to a constant head of 70 cm of water; after each set, R_1 was adjusted to increase the delivery.

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Book Review

HYDROGEN IONS: THEIR DETERMINATION AND IMPORTANCE IN PURE AND INDUSTRIAL CHEMISTRY. Volume II. By H. T. S. BRITTON, D.Sc., D.I.C., F.R.I.C. Fourth Edition. Pp. xx + 489. London: Chapman & Hall Ltd. 1956. Price 75s.

Those not already familiar with the Third Edition of "Britton's Hydrogen Ions" will find this volume weighted slightly on the side of industrial rather than pure chemistry. The subjects dealt with are: oxidation - reduction processes; titration in non-aqueous media; precipitation of hydroxides, basic chromates, borates, carbonates, silicates, sulphides and normal and basic phosphates; solutions of complex ions; analytical processes involving pH; pH control in the detection of metals with organic reagents; electro-deposition; tanning processes; sugar and paper manufacture; brewing; baking, water purification, corrosion and sewage disposal; ceramics; textiles; dyeing; ore flotation; and the pH of milk and hens' eggs.

This new edition of Volume II contains all the material presented in the Third Edition, the text being brought up to date by the inclusion of some 50 additions, sometimes of only a few lines, but usually of one or two paragraphs, with the exception that the chapter on the titration of acids and bases has been considerably enlarged. The result has been to increase the size of the book from 443 to 489 pages.

The complete revision of the chapter on titration in non-aqueous media will be particularly welcomed by analysts because of the growing use of this technique and a reliance that must be placed on pH equipment for a preliminary study of any new titration. On the other hand, analysts will not find the chapter "Analytical Processes Involving pH" of great value, since close control of pH in analytical processes is considerably more important to-day that it was 15 years ago, clearly owing to the increased availability of accurate pH meters.

Although automatic pH recording is mentioned in several places, no description is given of the equipment more recently available, probably because the author in general avoids the discussion of the commercial article.

This volume is still a valuable reference book and much of the information contained therein is of fundamental importance, but, with the majority of the references dated before 1940, one wonders if the industrial picture presented is truly representative of present-day practice.

A. G. JONES

Publications Received

CHROMATOGRAPHIC TECHNIQUES: CLINICAL AND BIOCHEMICAL APPLICATIONS. Edited by IVOR SMITH, B.Sc., Ph.D., F.R.I.C. Pp. xiv + 309. London: William Heinemann Medical Books Ltd. 1958. Price 45s.

THE UFAW HANDBOOK ON THE CARE AND MANAGEMENT OF LABORATORY ANIMALS. Edited by ALASTAIR N. WORDEN, M.A., B.Sc., M.R.C.V.S., F.R.I.C., and W. LANE-PETTER, M.A., M.B., B.Chir. Second Edition. Pp. xx + 951. London: The Universities Federation for Animal Welfare. 1957. Price 70s.

PURITY CONTROL BY THERMAL ANALYSIS. Proceedings of the International Symposium on Purity Control by Thermal Analysis, Amsterdam, 1957. Sponsored by the I.U.P.A.C. and organised by the Committee on Physico-Chemical Data and Standards. Edited by W. M. SMIT. Pp. xii + 182. Amsterdam: Elsevier Publishing Co.; London: Cleaver-Hume Press Ltd.; New York: D. Van Nostrand Co. Inc. 1957. Price 24s.; $4.85.

ORGANIC COLLOIDS. By BRUNO JIRGENSONS. Pp. xiv + 655. Amsterdam: Elsevier Publishing Co.; London: Cleaver-Hume Press Ltd.; New York: D. Van Nostrand Co. Inc. 1958. Price 85s.; $16.75.

BRITISH PHARMACOPOEIA 1958. Published under the Direction of the General Medical Council. Pp. xxvi + 1012. London: The Pharmaceutical Press. 1958. Price 63s.

PROGRESS IN STEREOCHEMISTRY. Volume II. Edited by W. KLYNE, M.A., D.Sc., Ph.D., and P. B. D. DE LA MARE, Ph.D., D.Sc. Pp. viii + 323. London: Butterworths Scientific Publications; New York: Academic Press Inc. 1958. Price 50s.; $8.80.

DISINFECTANTS: THEIR VALUES AND USES. By W. E. FINCH. Pp. 188. London: Chapman & Hall Ltd. 1958. Price 30s.

A MANUAL OF PAPER CHROMATOGRAPHY AND PAPER ELECTROPHORESIS. By RICHARD J. BLOCK, EMMETT L. DURRUM and GUNTER ZWEIG. Second Edition. Pp. xii + 710. New York and London: Academic Press Inc. 1958. Price $12.80; 91s. 6d.

STANDARD METHODS FOR TESTING PETROLEUM AND ITS PRODUCTS. Seventeenth Edition. February 1958. Pp. xxiv + 788. London: The Institute of Petroleum. 1958. Price 40s.

DIE METHODEN DER MIKROMASSANALYSE. By Professor Dr. JOSEF MIKA. Second Edition. Pp. xvi + 375. Stuttgart: Ferdinand Enke Verlag. 1958. Price (paper) DM 63; (cloth boards) DM 66.

A STRUCTURAL INTRODUCTION TO CHEMISTRY. By E. T. HARRIS, M.A., F.R.I.C. Pp. x + 181. London and Glasgow: Blackie & Son Ltd. 1958. Price 12s. 6d.

STANDARD METHODS FOR TESTING TAR AND ITS PRODUCTS. Fourth Edition. Pp. xxvi + 585. Gomersal, nr. Leeds: Standardization of Tar Products Tests Committee. 1957. Price 42s., postage 1s. 9d. extra.

QUALITATIVE TESTING AND INORGANIC CHEMISTRY. By JOSEPH NORDMANN. Pp. xii + 488. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1957. Price $6.25; 50s.

TRACE ANALYSIS. Edited by JOHN H. YOE, M.S., M.A., Ph.D., and HENRY J. KOCH, JUN., A.B., M.D. Pp. xiv + 672. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1957. Price $12.00; 96s.

EMULSIONS: THEORY AND PRACTICE. By PAUL BECHER. Pp. x + 382. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1957. Price $12.50; 100s.

American Chemical Society Monograph No. 135.

Errata

MARCH (1958) ISSUE, p. 136, 5th line of text. *For* "that have widely different major constituents" *read* "of widely varying major compositions."

IBID., p. 136, 18th line of text. *For* "constituents" *read* "compositions."

THE SOCIETY FOR ANALYTICAL CHEMISTRY

FORMERLY THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

FOUNDED 1874. INCORPORATED 1907.

THE objects of the Society are to encourage, assist and extend the knowledge and study of analytical chemistry by holding periodical meetings, by promoting lectures, discussions and conferences, and by the publication of a journal devoted to all branches of analytical chemistry; to study questions relating to the analysis, nature and composition of natural and manufactured materials generally; and to promote, or assist to promote, the efficiency and the proper administration of the laws relating to the control and composition of such materials.

The Society includes members of the following classes:—(*a*) Ordinary Members who are persons of not less than 21 years of age and who are or have been engaged in analytical, consulting or professional chemistry; (*b*) Junior Members who are persons between the ages of 18 and 27 years and who are or have been engaged in analytical, consulting or professional chemistry or *bona fide* full-time or part-time students of chemistry. Each candidate for election must be proposed by three Ordinary Members of the Society who shall provide written testimony of their personal knowledge as to his scientific and professional fitness. If the Council in their discretion think fit, such testimony may be dispensed with in the case of a candidate not residing in the United Kingdom. Every application is placed before the Council and the Council have the power in their absolute discretion to elect candidates or to suspend or reject any application. Subject to the approval of Council, any Junior Member above the age of 21 may become an Ordinary Member if he so wishes. A member ceases to be a Junior Member on the 31st day of December in the year in which he attains the age of 27 years. Junior Members may attend all meetings, but are not entitled to vote.

The Entrance Fee for Ordinary Members is £1 1s. and the Annual Subscription is £3 3s. Junior Members are not required to pay an Entrance Fee and their Annual Subscription is £1 1s. No Entrance Fee is payable by a Junior Member on transferring to Ordinary Membership. The Entrance Fee (where applicable) and first year's Subscription must accompany the completed Form of Application for Membership. Subscriptions are due on January 1st of each year.

Scientific Meetings of the Society are usually held on the first Wednesday in October, November, December, February, April and May, in London, but from time to time meetings are arranged in other parts of the country. The Annual General Meeting is usually held in London on the first Friday in March. Notices of all meetings are sent to members by post.

All members of the Society have the privilege of using the Library of The Chemical Society. Full details about this facility can be obtained from the Librarian, The Chemical Society, Burlington House, Piccadilly, London, W.1.

The Analyst, the official organ of the Society, is issued monthly, to all Ordinary and Junior Members, and contains reports of the proceedings of the Society, original papers and notes, information about analytical methods, Government reports and reviews of books. In addition, all Ordinary Members receive *Analytical Abstracts*, providing a reliable index to the analytical literature of the world.

Forms of application for membership of the Society may be obtained from the Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1.

LOCAL SECTIONS AND SUBJECT GROUPS

THE North of England, Scottish, Western and Midlands Sections were formed to promote the aims and interests of the Society among the members in those areas. The Microchemistry, Physical Methods and Biological Methods Groups have been formed within the Society to further the study of the application of microchemical, physical and biological methods of analysis. All members of the Society are eligible for membership of the Groups.

The Sections and Groups hold their own meetings from time to time in different places. There is no extra subscription for membership of a Section or Group. Application for registration as a member should be made to the Secretary.